REMARKS

The Applicants appreciate the Examiner's very quick and courteous Action.

Claims 1-9, 11-14, 16-27, 29, and 31-33 are pending in the application. Claims 1-33 stand rejected. Claims 7, 9, 12, 14, 16, 17, 27, 29 and 32 are amended herein; no new matter has been added. Claims 10, 15, 28 and 30 have been canceled.

Claim 7 has been amended to correct an inadvertent error in antecedent basis since claim 8 dependent thereon refers to a mineral acid, but no mineral acid was recited in claim 7. This amendment has been made to correct an inadvertent error and not for any reason substantially related to patentability.

The Applicants respectfully request reconsideration in view of the following remarks.

Rejection Under 35 U.S.C. §103 over Crump, et al.

The Examiner has again rejected composition claims 9-21 and 27-33 under 35 U.S.C. §103(a) as allegedly being unpatentable over U.S. Pat. No. 5,389,594 to Crump, et al. for reasons of obviousness.

The Examiner finds that Crump discloses chelants used in oil drilling that comprise one of citric acid, glyceric acid, gluconic acid, or glycollic acid, such chelants being useful in water. The oil/chelant mixture is contended by the Examiner to further comprise sulfuric acid to reduce the pH of the mixture to about 4.2. The amount of chelant in the wash water is seen by the Examiner to be about 0.01 to about 40 weight percent and corrosion inhibitors are included in the composition. See Crump, column 1, lines 16-27, column 11, lines 57-65, column 13, lines 22-29 and 57-64, column 14, lines 1-14, and column 16, lines 27-50. Presumably, the Examiner concludes that the rejected composition claims are obvious from these disclosures of Crump, et al.

In response to the Applicants' Amendment, the Examiner notes that Applicants' first argument is that Crump only very generally discloses the prior art chelants and that (supposedly) they may be useful in a long list of applications. Therefore, Applicant argues that the Crump reference does not teach

that the chelants of the invention are used in oil drilling operations. However, the Examiner finds that Crump discloses that chelants in general and the chelants of the invention of Crump are useful in oil field operations (see Crump, column 1, lines 16-27 and column 5, lines 40-59). Therefore, the Examiner contends that it would be obvious to use the chelants of citric acid, glyceric acid, gluconic acid, or glycollic acid in oil field operations, because Crump teaches that chelants are useful in oil field operations.

The Examiner finds that Applicants' second argument is that Crump provides no motivation to combine the mineral acids to the chelant mixture. However, Crump discloses that sulfuric acid aids in recycling used chelants (see Crump, column 11, lines 57-66). Therefore, the Examiner contends that it would be obvious, in light of Crump, that a recycled chelant could contain sulfuric acid.

The Applicants respectfully traverse.

Applicants would *again* respectfully point out that dependent claim 21 is a *method* claim depending from independent method claim, and thus is not a composition claim like the rest of the claims in the rejected group.

To support an obviousness rejection, the Examiner has the initial burden of establishing a *prima facie* case of obviousness of the pending claims over the cited prior art, *In re Oeticker,* 977 F.2d 1443, 1445; 24 U.S.P.Q.2d 1443 (Fed. Cir. 1992). As will be concluded below, the Examiner has not established a *prima facie* case of obviousness of the composition claims based on Crump, et al. alone.

Claims 9, 11 and 27 now recite a composition for transferring metals and/or amines from a hydrocarbon phase to a water phase that comprise water, a water-soluble hydroxyacid *and a mineral acid,* and at least one additional *component selected from the group consisting of a water or alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof,* where the pH of the composition is 6 or below. Support for the amendments herein is found in dependent claims 10 and 28 as originally filed,

and thus the inclusion of this new language in the independent claims does not constitute improper insertion of new matter. Dependent claims 10 and 28 are canceled as redundant.

Claims 12-13 now recite a composition for transferring metals and/or amines from a hydrocarbon phase to a water phase that comprise water, a water-soluble hydroxyacid and a *demulsifier*, where the pH of the composition is 6 or below.

Claims 14-20 and 29-33 all relate to treated crude oil emulsions where *crude oil* is a required component of the treated emulsions. A water-soluble organic acid and a wash water where the pH of the wash water is 6 or below are also recited. Independent claims 14 and 29 have been amended to additionally recite a *mineral acid*. Support the amendments to these claims is found in dependent claims 15 and 30 as originally filed, and thus these amendments do not constitute improper insertion of new matter. Dependent claims 15 and 30 are canceled as redundant.

The Applicant respectfully submits that none of these compositions, as amended, are obvious from Crump, et al. Crump, et al. discloses certain new degradable chelants having sulfonate groups (title and Abstract therein) which are not at issue here. The Examiner contends that Crump, et al. discloses chelants in oil drilling and alleges that such chelants may be citric acid, glyceric acid, gluconic acid, or glycolic acid and that it is obvious to include such chelants in compositions such as the above, but the Applicants respectfully submit that this is factually incorrect.

In truth, the reference only very generally discloses that prior art chelants and chelants of their invention might be useful in a long list of applications – none of which relate to the *refinery desalting* processes and compositions herein. Refinery processes and compositions are not the same as or related to oil drilling operations. Indeed, because Crump, et al. has no teaching or suggestion relating to refinery desalting processes or compositions used therein, the Applicants respectfully submit that it should be withdrawn as a non-analogous document. Non-analogous art is not properly prior art; the

examiner cannot pick statements out of their proper context. *In re Pagliaro,* 657 F.2d 1219, 1225; 210 U.S.P.Q. 888, 892 (C.C.P.A. 1981). If the teaching is outside the art area, it must be shown that a person of ordinary skill would have considered it. *Ex parte Murphy and Burford,* 217 U.S.P.Q. 479, 482 (Bd. of App., 1982). Crump, et al. concerns novel chelants useful primarily in detergent compositions. The Applicants respectfully submit that there is no evidence of record suggesting, teaching or hinting that one having ordinary skill in the art of refinery desalters would consider Crump, et al. as useful for anything relevant.

In the portions of Crump, et al. that the Examiner notes as specifically reciting citric acid, glyceric acid, gluconic acid, or glycolic acid (column 16, lines 27-50), no mention is made of a particular application or use, much less (1) compositions that have mineral acids, (2) compositions having crude oil or (3) compositions having an additional component that is an alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof, especially a demulsifier. In particular, the Examiner's attention is respectfully directed to column 1, lines 16-27 noted by the Examiner:

> Chelants are used in a variety of applications including
> food processing,
> soaps,
> detergents,
> cleaning products,
> personal care products,
> pharmaceuticals,
> pulp and paper processing,
> water treatment,
> metalworking and metal plating solutions,
> textile processing solutions,
> fertilizers,
> animal feeds,
> herbicides,
> rubber and polymer chemistry,
> photofinishing, and
> *oil field chemistry.*
> Some of these activities result in chelants entering the environment. For instance, agricultural uses or detergent uses may result in measurable quantities of the chelants being in water. It is, therefore, desirable that chelants degrade after use. (Emphasis added.)

Oil field chemistry is only listed at the end of a very long list of applications, and no specific utility within the broad field of oil field chemistry is given, nor are any particular chelants suggested, supposed or hinted at for *any* of these very general application classes. Further, oil field chemistry is different from refinery chemistry and processes which are downstream from the oil field. In another instance at column 5, lines 40-59, Crump, et al. notes for his *novel* chelants:

> Chelants *of the invention* are useful, for instance,
> in food products vulnerable to metal-catalyzed spoilage or discoloration;
> in cleaning and laundering products for removing metal ions, e.g. from hard water, that may reduce the effectiveness, appearance, stability, rinsibility, bleaching effectiveness, germicidal effectiveness or other property of the cleaning agents;
> in personal care products like creams, lotions, deodorants and ointments to avoid metal-catalyzed oxidation and rancidity, turbidity, reduced shelf-life and the like;
> in pulp and paper processing to enhance or maintain bleaching effectiveness;
> in pipes, vessels, heat exchangers, evaporators, filters and the like to avoid or remove scaling,
> in pharmaceuticals;
> in metal working;
> in textile preparation, desizing, scouring, bleaching, dyeing and the like;
> in agriculture as in chelated micronutrients or herbicides;
> in polymerization or stabilization of polymers;
> in photography, e.g. in developers or bleaches;
> in the *oil field such as for drilling, production, recovery, hydrogen sulfide abatement and the like.* (Emphasis added.)

However, as noted, these applications relate to the chelants of the Crump, et al. invention. The claims herein do not encompass the Crump, et al. inventive chelants, only the recited water-soluble hydroxyacids, so column 5, lines 40-59, Crump, et al. is not appropriate or relevant to the invention claimed herein, only the column 1, lines 16-27, teaching is and as noted this section is only a very general, amorphous list of potential applications – none of which are concerned with refineries or refinery desalters.

Additionally, and most importantly, oil field applications are _not_ refinery applications. Refinery desalting processes and applications, addressed by the present invention, relate to refinery operations. Oil field operations are not refinery operations. Oil field operations take place in the oil field and concern operations such as those listed above _e.g._ "drilling, production, recovery, hydrogen sulfide abatement and the like". As will be established more particularly in the discussion of the next rejection, to which the Examiner's attention is respectfully directed, refinery operations take place at different locations from and concern different issues than oil field operations. There is nothing in Crump, et al. about refinery operations and compositions useful therein, and thus Crump, et al. can teach or suggest nothing about them.

Further, simply because the novel Crump, et al. chelants are taught as useful for the column 5 applications, there is no reason to suppose or suspect that the more conventional, prior art chelants would have any utility at all for the applications _not in_ column 5. Crump, et al. discloses and mentions no particular organic compound for any particular application – except for detergent formulations. Crump, et al. give no examples relating to any oil field chemistry, much less any applications that relate to compositions of the subject claims (except detergent formulations) – and even less for refinery operations. The examples given relate to laundry detergents and the biodegradability thereof. Indeed, the Crump, et al. teachings quoted by the Examiner in columns 13 and 14 only relate to cleaning formulations, washing compositions, and detergent formulations.

With respect to composition claims 9, 11 and 27, it is true that the mineral acid sulfuric acid is mentioned in column 11, lines 57-66 of Crump, et al., but this is only in the context of replenishing the lower valence metal chelate – please see column 11, lines 59-60, preferably done by electrochemical regeneration – please see particularly column 11, line 67 to column 12, line 19. (Applicants are sure the Examiner is aware that electrochemical regeneration is not the same as electrostatic coalescence, to be discussed with respect to the method claims, _infra_.) A composition, as claimed of water, water-soluble hydroxyacids _together_

with a mineral acid and *at least one additional component selected from the group consisting of an alcohol solvent, a corrosion inhibitor, a demulsifier, a scale inhibitor, metal chelants, wetting agents and mixtures thereof* is *not* disclosed or taught by the Crump, et al. reference (for replenishing or any other purpose). Crump, et al. only discloses such acids to be present with their novel chelants in a replenishing or regeneration procedure. Note that the additional component in the amended claims that may be a metal chelant is different from the water-soluble hydroxyacids already recited in these composition claims. Further Crump, et al. mentions corrosion inhibitors and alcohols, but only as optional components in *detergent formulations*; please see column 14, lines 1-35 and column 19, lines 36-43.

With respect to composition claims 12 and 13, Crump, et al. does not teach or suggest the recited composition of water, at least one of the recited water-soluble hydroxyacids and a demulsifier. Crump, et al. does disclose detergent compositions which may contain water and some optional components, but Crump, et al. does not suggest any compositions containing a demulsifier; indeed, demulsifiers are not mentioned in Crump, et al. In fact, since Crump, et al. is focused on detergent formulations, demulsifiers would be counter-productive and opposed to the goals of a detergent formulation.

With respect to composition claims 14, 16-20, 29, and 31-33; these claims are now directed to treated hydrocarbon crude oil emulsions that contain: crude oil, a composition comprising water-soluble hydroxyacids, a wash water with a pH of 6 or below, and a mineral acid. Crump, et al. cannot teach or suggest anything about such compositions because (1) Crump, et al. does not mention or suggest crude oil, (2) Crump, et al. does not mention or suggest refinery operations, much less refinery desalter operations, which is where such compositions would occur, (3) the wash water recited in the pending claims is not the same as the wash water employed in Crump, et al.'s detergent formulations ("washing" crude oil and washing clothes are very different), and (4) the only place Crump, et al. mentions a mineral acid is in connection with replenishing his novel chelants. Crump, et al. makes no mention of or hint at crude oil, refinery operations, wash water for

refinery operations or replenishing the water-soluble hydroxyacids recited in the instant claims.

The Applicants respectfully submit that at best Crump, et al. supposes an entire research program to try their chelants, not necessarily the known organic compounds, in each of the broad applications listed – *none* of which include or encompass refinery desalting operations, indeed "oil field chemistry" does not overlap "refinery chemistry". Refinery operations occur *after and subsequent to* the oil field operations merely mentioned in Crump, et al. The USPTO Board of Patent Appeals and Interferences stated in the case of *Ex Parte Obukowicz*, 27 U.S.P.Q.2d 1063 (B.P.A.I. 1992) that a prior art reference that only gives general guidance and is not at all specific as to the particular form of the claimed invention and how to achieve it may make a certain approach "obvious to try" but does not make the claimed invention obvious, citing *In re O'Ferrell*, 853 F.2d 894, 7 U.S.P.Q.2d 1673, 1681 (Fed. Cir. 1988). "Obvious to try" has long been held not to constitute obviousness, *In re O'Farrell*, 853 F.2d 894, 903, 7 U.S.P.Q.2d 1673, 1680-81 (Fed. Cir. 1988). A general incentive does not make obvious a particular result, nor does the existence of techniques by which those efforts can be carried out, *In re Deuel*, 51 F.3d 1552, 1559, 34 U.S.P.Q.2d 1210 (Fed. Cir. 1995). Thus, for this reason alone, the Applicants respectfully submit that a *prima facie* obviousness rejection has not been made.

The recent *KSR v. Teleflex* U.S. Supreme Court case addressed "obviousness to try".

> The same constricted analysis led the Court of Appeals to conclude, in error, that a patent claim cannot be proved obvious merely by showing that the combination of elements was "obvious to try." *Id.*, at 289 (internal quotation marks omitted). When there is a design need or market pressure to solve *a problem* and there are *a finite number of identified, predictable solutions,* a person of ordinary skill has good reason to pursue the known options within his or her technical grasp. If this leads to the anticipated success, it is likely the product not of innovation but of ordinary skill and common sense. In that instance the fact that a combination was obvious to try might show that it was obvious under §103. *KSR International Co. v. Teleflex, Inc.* 550 U.S. ___ 17, 127 S.Ct. 1727 (April 2007) slip opinion (Emphasis added.)

This decision involved the obviousness of a mechanical, adjustable accelerator pedal for vehicles where there were references and patents concerned with the pivot points of the pedals and sensors therefore. However, the situation here is not that in *KSR v. Teleflex* because there is not simply "a" single problem in providing a mechanical accelerator having an adjustable position with respect to the driver. Instead, there is a long list of merely supposed, potential applications: food processing, soaps, detergents, cleaning products, personal care products, pharmaceuticals, pulp and paper processing, water treatment, metalworking and metal plating solutions, textile processing solutions, fertilizers, animal feeds, herbicides, rubber and polymer chemistry, photofinishing, and *oil field chemistry.* Furthermore, there is not "a finite number of identified, predictable solutions", but rather instead a very large, nearly infinite number of prior art chelants and organic compounds that might or *might not* work in each of very large list of applications. Additionally, none of the supposed applications merely listed in Crump, et al. relate to refinery operations, much less desalter operations.

More specifically, Crump, et al. gives *no* help to one of ordinary skill in the art about *which* chelants and/or organic compounds, much less that the recited hydroxyacids which may nor may not function as chelants in the claimed methods, *should* be used in *which* applications, much less which chelants are to be used with *mineral acids* and additional components to give the compositions of claims 9, 11 and 27. Further, Crump, et al. gives no suggestion, hint or motivation about *which* chelants and/or organic compounds, much less that the clamed hydroxyacids, *should* be used in compositions that also contain a *demulsifier* as recited in claims 12-13. And in particular, Crump, et al. presents no motivation, hint or suggestion about *which* conventional chelants, much less which of the recited hydroxyacids, should be used in crude oil emulsions where *crude oil* is a required component of the treated emulsions as recited in claims 14-20 and 29-33 herein. Indeed, the term "crude oil" is used nowhere in Crump, et al., and the Applicants respectfully submit that it is particularly impossible for this latter group of claims to be obvious from the Crump, et al. disclosure since the reference does

not so much as mention crude oil, much less crude oil together with water, the recited water-soluble hydroxy acids and a mineral acid.

Finally, the Applicants respectfully submit that Crump, et al. does not simply disclose citric acid, glyceric acid, gluconic acid, or glycolic acid, but rather a much longer list of organic chelants at column 16, lines 27-50:

> Further organic compounds which act as chelants for calcium and may be present in detergent formulations are *polycarboxylic acids, hydroxcarboxylic* [sic] *acids and aminocarboxylic acids* which are usually used in the form of their water-soluble salts.
>
> Examples of polycarboxylic acids are *dicarboxylic acids of the general formula HOOC—(CH₂)ₘ—COOH where m is 0-8,* and also *maleic acid, methylenemalonic acid, citraconic acid, mesaconic acid, itaconic acid, noncyclic polycarboxylic acids having 3 or more carboxyl groups in the molecule, e.g. tricarballylic acid, aconitic acid, ethylenetetracarboxylic acid, 1,1,3-propanetetracarboxylic acid, 1,1,3,3,5,5-pentanehexacarboxylic acid, hexanehexacarboxylic acid, cyclic di- or poly-carboxylic acids, e.g. cyclopentanetetracarboxylic acid, cyclohexanehexacarboxylic acid, tetrahydrofurantetracarboxylic acid, phthalic acid, terephthalic acid, benzene-tricarboxylic, -tetracarboxylic or -pentacarboxylic acid and mellitic acid.*
>
> Examples of *hydroxymonocarboxylic and hydroxypolycarboxylic acids are glycollic acid, lactic acid, malic acid, tartronic acid, methyltartronic acid, gluconic acid, glyceric acid, citric acid, tartaric acid and salicylic acid.* (Emphasis added.)

Crump, et al. does not identify or suggest *which* of these organic compounds are suitable or even might be suitable for *which* of the many applications merely mentioned, much less in compositions containing mineral acids, crude oil or one of the additional components. Applicants respectfully submit that one can find most of the components listed in Crump, et al. in the Chemical Marketing Reporter or the CAS listing of chemical compounds as well, but that does not tell one having simply *ordinary* skill in the art which one to use in which composition or in *which* application or *how* to select it – and neither does Crump, et al.

The Applicants respectfully submit further that in chemical cases it is often not predictable which chemical compound in a list of potential candidates are suitable in a particular application. Where no more direction is given about which particular prior art organic compounds would work for any of the specific

applications merely mentioned in the reference (and for some unknown reason discounting the novel chelates touted by Crump, et al.), it must be concluded that it is not predictable or obvious which such chelates would work at all in any given use or method or composition. Indeed, Crump, et al. themselves indicate that factors such as chelant capacity do not directly indicate the effectiveness of a chelant. The Examiner's attention is respectfully directed to column 5, lines 1-6:

> *Chelating capacity is not, however, a direct indicator of effectiveness in activities* such as stabilizing bleach. For instance, hydroxy-ethyliminodiacetic acid (HEIDA) is effective in chelating, e.g. copper (294 mg copper per gram of chelate), but is relatively *ineffective* in stabilizing bleaches. (Emphasis added.)

Thus, even the sole reference in the instant rejection concedes that not all of the chelants mentioned therein are useful in all applications mentioned therein.

The Applicants respectfully submit that for all of these reasons a *prima facie* obviousness rejection of these composition claims, as amended, has not been made.

Rejection Under 35 U.S.C. §103 over Reynolds, et al. in view of Crump, et al.

The Examiner has again rejected claims 1-8 and 22-25 under 35 U.S.C. §103(a) as allegedly being unpatentable over U.S. Pat. No. 4988433 to Reynolds, et al. in view of Crump, et al. for reasons of obviousness.

The Examiner finds that Reynolds discloses a method of transferring metals from a crude oil to a water phase including contacting the oil with water that already includes the chelant. The pH of the mixture is adjusted so that it remains above 2. See Reynolds, column 3, lines 12-39. The Examiner also finds that Reynolds discloses the electrically directed precipitation of metals (see Reynolds, column 1, lines 49-65).

The Examiner admits that Reynolds does not disclose the chelating compounds claimed.

However, the Examiner contends that Crump discloses chelants used in oil drilling that comprise one of citric acid, glyceric acid, gluconic acid, or glycollic

acid, such chelants being useful in water. The oil/chelant mixture further comprises sulfuric acid to reduce the pH of the mixture to about 4.2. The amount of chelant in the wash water is about 0.01 to about 40 weight percent and corrosion inhibitors are included in the composition. See Crump, column 1, lines 16-27, column 11, lines 57-65, column 13, lines 22-29 and 57-64, column 14, lines 1-14, and column 16, lines 27-50.

Further, the Examiner alleges that Crump discloses that such chelants are useful in oil drilling and production (see Crump, column 5, lines 40-59).

Therefore, the Examiner concludes that it would have been obvious to one having ordinary skill in the art at the time of the invention to modify the process of Reynolds to include chelants used in oil drilling that comprise one of citric acid, glyceric acid, gluconic acid, or glycollic acid in order to use chelants that are useful in oil drilling and production.

In response to the Applicants' Amendment, the Examiner finds that the Applicants' third argument is that Reynolds in view of Crump does not disclose electrostatic coalescence. However, Reynolds also discloses the electrically directed precipitation of metals (see Reynolds, column 1, lines 49-65).

The Applicants must again respectfully traverse.

To support an obviousness rejection, the Examiner has the initial burden of establishing a *prima facie* case of obviousness of the pending claims over the cited prior art, *In re Oeticker, id*. As will be shown below, the Examiner has not established a *prima facie* case of obviousness based on Reynolds, et al. in view of Crump, et al.

The Applicants stipulate that Reynolds, et al. does use a desalting process to remove metals and does claim acetic acid. Applicants respectfully submit that the only other example given is benzoic acid. Thus, Reynolds, et al. are specific to monobasic acids. As the Examiner admits, there is no claim or teaching to the water-soluble hydroxyacids required by the instant method claims.

The Examiner in responding to the Applicants' previous amendment also contends that Reynolds, et al. discloses "the electrically-directed precipitation of metals" – however this excerpt is only present as a brief description of U.S. Pat. No. 3,153,623 to Eldib, et al., which is prior art to Reynolds, et al. The Reynolds, et al. reference itself does not include or incorporate such "electrically-directed precipitation of metals". In fact, Reynolds, et al. merely mentions this aspect in brief discussions of a variety of prior art patents, and Reynolds, et al. does *not* even suggest or teach using such "electrically-directed precipitation of metals" in their own method, much less teach or suggest using it in or for any other method. In fact, by merely listing this technique as a prior one that they apparently consider and <u>do not use</u>, they teach away from it, and conversely certainly do not teach toward it. For this reason alone, the Applicants respectfully submit that the rejection should be withdrawn.

Crump, et al. does not provide the deficiencies of Reynolds, et al. for many reasons. As noted previously, Crump, et al. only discloses a very long list of prior art organic compounds and does not illuminate or suggest that the recited water-soluble hydroxyacids from the very large group listed are suitable or acceptable for *any particular* application, except detergent applications, cleaning or washing compositions, much less the claimed methods of transferring metals and/or amines from a hydrocarbon phase to a water phase in any context, much less in the recited refinery desalting processes.

Indeed, Crump, et al. teaches in a completely different direction from that claimed. Crump, et al. teaches that their novel chelants may be part of *detergent formulations* with other components. The claimed methods and compositions *do not* and *should not* include detergent materials (soaps), binders, oxidants and so on. One of even ordinary skill in the refinery desalter art would never use a soap in refinery desalting applications. Soaps create problems by generating stable emulsions in the refinery desalter when crude oil and water are mixed. A typical soap seen in refining of crude oil is a metal naphthenate. The Examiner's

attention is respectfully directed to the enclosed article C. Phillips, Jr., "Treatment of Refinery Emulsions and Chemical Wastes," *Industrial and Engineering Chemistry,* 1954, Vol. 46, No. 2, pp. 300-303, which notes in the Abstract at the top of page 301:

> Major contributors to the poor condition of waste waters from petroleum *refineries* are naphthenic and sulfonic acids, either as free acids or as converted water-soluble salts in the sewer systems. These oily salts or *soaps* form oil-water emulsions that clog gravity-type separators. Water from crude oil desalters contains high concentrations of calcium and magnesium salts, which in an alkaline medium precipitate in the sewers and function as finely divided solid *emulsion stabilizers.* (Emphasis added.)

The Examiner's attention is also respectfully directed to the enclosed article D. Arla, et al., "Influence of pH and Water Content on the Type and Stability of Acidic Crude Oil Emulsions," *Energy & Fuels,* 2007, Vol. 21, pp. 1337-1342, particularly the Abstract:

> Dependent upon the conditions of pH and water content, an *acidic crude oil may form different type of emulsions with different stability.* These oils generally contain large amounts of naphthenic acids, RCOOH, which result from crude oil biodegradation. They also contain heavier compounds such as asphaltenes and resins. *All of these amphiphiles may contribute to the formation and stability of emulsions.* ... The *stability of oil-in-water emulsions is ensured by electrostatic repulsion between the naphthenates,* RCOO⁻, present at the interface, whereas *that of water-in-oil emulsions is due to the amphiphiles contained in the heavy fraction,* i.e., asphaltenes and resins. (Emphasis added.)

The instant method claims use the recited composition in *refinery desalters.* Crump, et al. mentions only "oil field chemistry" or use in oil field production etc. Oil field chemistry and oil field production have nothing to do with refineries. The Examiner appears to assume that Crump, et al. is talking about use with emulsions such as those in refinery desalters, but the language is not specific and is more likely referencing the appearance of the well head as much as it is dealing with the crude oil – but refineries are not mentioned, much less

desalters. Even if one having ordinary skill in the art would somehow make the connection between oil field technology and the claimed refinery desalter application, which the Applicants are not conceding, the two processes are different. Oil field produced fluids contain higher amounts of water than used in the desalting process and water is typically only removed from the oil and not added intentionally with high shear to make emulsions as is done in refinery applications. The articles mentioned above talk about soaps (metal naphthenates) and the problems (stable emulsions) they cause. One of even ordinary skill in the refinery desalter technology would never have soaps added to desalter materials, since the point is to separate out species, not bind them more tightly together.

More specifically with respect to Crump, et al.:

At column 1, line 16-27 and column 5 lines 40-59 of Crump, et al., no reference is made to a desalting process. These sections only indicate chelants are used in *oil field* applications but one is not told if it is corrosion inhibition, scale inhibition or some other use. There is no reference, teaching, suggestion or hint to the claimed chemistry or to a refinery and particularly no mention of a desalter-type application. A desalter application typically *adds water* to a crude oil and uses a mix valve to *create an emulsion* while an oil field application *removes water* while trying to *break emulsions.* Oil field separators typically use gravity to separate produced fluids. A desalter uses electricity in addition to heat and water intentionally added to the crude oil. The Examiner's attention is respectfully directed to the enclosed excerpt from J. H. Gary, et al., Petroleum Refining, Marcel Dekker, 2001, Chapter 4 "Crude Distillation", pages 37-50, particularly page 46. Desalters are *not* used in oil field applications since the produced fluids contain higher amounts of water and there is no need to reduce salt content of the crude oil. The *Petroleum Refining* reference states a typical % wash water rate is 3-10% (page 46). Produced fluids typically contain high amounts of water.

Column 11, lines 57-65 of Crump, et al. This portion of Crump, et al. does not apply to refineries, desalting or even oil field applications. It does not treat crude oil and only relates to NOx removal from flue gas. It only uses sulfuric

acid or electrochemistry to reduce the metal to a lower oxidation state. The acid or electrochemistry does nothing to the chelant and is designed to recover the metal which is not part of the Applicants' process. Desalters do not change the oxidation state of the metal as described in this section. The reference also does not include emulsions or other materials in our application. The electrochemistry described has nothing to do with electrostatic coalescence of the method claims herein.

Column 13, Lines 22-29 and 57-64 and column 14, lines 1-14 of Crump, et al. These portions of Crump, et al. indicate that the compounds of their invention (Formula I) can be used in a cleaning formulation. As mentioned earlier, the claimed desalter formulations do not contain detergents, builders, oxidizers or other materials for the reasons stated above, and the methods do not employ such materials. This is evident to one having ordinary skill in the art by the fact that a refinery desalting process is required as recited in the claims. The amounts mentioned in these excerpts do not matter as it is a formulation that is different than recited in the claims as amended. Further, lines 65-69 of column 13 of Crump, et al. state a pH of between 8 and 12 which is outside the recited pH of the wash water of 6 or below. Applicants further doubt that anyone will want to wash their clothes in a mixture of 90% crude oil and 10% water and hope to have successful cleaning -- Crump, et al. primarily focused on detergent formulations, particular in columns 13 and 14.

Column 16, lines 27-50 of Crump, et al. These lines mention some of the acids in the instant claims. However, this portion of Crump, et al. merely states that these components may be added to the detergent formulation in addition to the other chelants. The glycolic acid is just part of a much bigger formulation and as mentioned earlier, many of the components Crump, et al. teach for their detergent formulations are not wanted or desired in the compositions and methods claimed herein. Binders cause scale formation, detergents stabilize emulsions and oxidizers (bleach) will either chlorinate hydrocarbons (to generate toxic materials for the waste water treatment plant) or oxidize (peroxide) them to materials like carboxylic acids which are potential soaps.

Furthermore, as also settled in the discussion of the rejection based on Crump, et al. alone, above, Crump, et al. discloses a lengthy list of supposed uses and applications for the prior art chelants – without so much as hinting *which* chelants would be suitable for *which* applications. At best, the supposed combination of Reynolds, et al. with Crump, et al. might be for a very large research program to try to identify which of the novel Crump, et al. chelants would be useful in the Reynolds, et al. hydrocarbonaceous feedstocks demetalation – it is respectfully submitted that there would be even *less* motivation to consider using the *conventional* organic compounds in the Reynolds, et al. method since one having ordinary skill in the art reviewing both references would be more inclined to use the new and novel chelants of Crump, et al. – but these are not the water-soluble hydroxyacids recited in the claims at issue.

Finally, all of the method claims subject to the present rejection recite "using electrostatic coalescence". The closest that the Reynolds, et al. reference comes is the mention of "electrically-directed precipitation of metals" noted only with respect to the prior U.S. Pat. No. 3,153,623 to Eldib, et al., a teaching not incorporated by Reynolds, et al. in their method and thus apparently not valued or found useful. Thus, for this reason alone the method claims which require "using electrostatic coalescence" cannot be obvious from the references taken together. The Applicants respectfully submit that for this reason alone, a *prima facie* obviousness rejection of the method claims has not been made. Where is the teaching, suggestion or motivation *in the references* for *incorporating* electrostatic coalescence?

The Applicants further respectfully submit that for all of the reasons established above, especially taken together, a *prima facie* obviousness rejection of the method claims has not been made.

Request for Entry of Amendment

The Applicants would respectfully request that the instant Amendment be entered under 37 CFR §1.116(b): "Amendments presenting rejected claims in better form for consideration on appeal may be admitted." It is respectfully noted
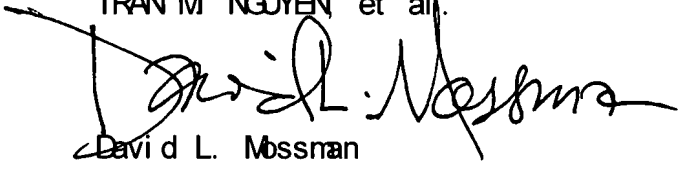
that the composition claims have been narrowed, and that claims have been canceled herein. More specifically, the remaining composition claims 9, 11-14, 16-20, 27, 29 and 31-33 have a more narrow and precise recitation of components that narrows and clarifies them. It is respectfully submitted that for all of these reasons, which simplify and narrow the issues, the instant Amendment should be entered, which will place the claims in better form for consideration in a Pre-Appeal Brief Review, and for Appeal in general.

Further, the Applicants would respectfully submit that the instant amendment be entered under 37 CFR §1.116(c): "If amendments touching the merits of the application or patent under reexamination are presented after final rejection, or after appeal has been taken, or when such amendment might not otherwise be proper, they may be admitted upon showing of good and sufficient reasons why they are necessary and were not earlier presented." The Applicants submit that the reason why the amendments above and arguments below are necessary and were not earlier presented is simply because Applicants had a *bona fide* belief that the Examiner would understand that Crump, et al. is an inappropriate reference for the claims at issue, and would be withdrawn. Further, prior to the present Amendment, the Applicants did not understand why the Examiner supposed that Reynolds, et al. was at all concerned with electrically directed precipitation of metals, and only now has had a chance to address this point. For the Applicants to have any hope of being assured of a chance to address the instant rejections and fully discuss and explore the Crump, et al. reference, the amendments and arguments herein must be entered and considered.

It is respectfully submitted that the arguments presented above overcome the rejection. Reconsideration and allowance of the claims are respectfully requested. The Examiner is respectfully reminded of his duty to indicate allowable subject matter. The Examiner is invited to call the Applicants' attorney at the

number below for any reason, especially any reason that may help advance the prosecution.

Respectfully submitted,
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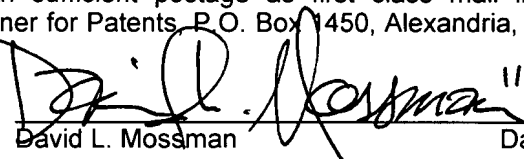
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Three types of control chemicals, including liquid chlorine, copper sulfate, and sodium hypochlorite, were employed during field investigations, as well as combinations of liquid chlorine with copper sulfate.

Chlorination of the plant salt water system (raw water) apparently has little effect on separator slime growth. Slug chlorination (applied at 20 p.p.m. for 2 hours, three times daily) gave intermittent residuals after passage through some process equipment, such as heat exchangers, but not through barometric condensers, which carry the main process waste to the separator.

Chlorination of the separator waste, with chlorine, at the inlet, outlet, and at both points simultaneously was studied, with both continuous and intermittent application. All types of dosing to a measurable residual were effective in dislodging at least some growth. Effluent velocity at normal flow was 0.22 foot per second, that in the open ditch 0.10 foot per second, and average velocity from separator to bay 0.17 foot per second. These velocities were significantly below scour rates of flow and dislodgement of growth was entirely attributed to applied chlorine. Shock treatment to high residuals caused bleaching and maximum sloughing, but some bleached growths remained attached in the flume and ditch, even at 800 p.p.m. residual. Dead growths that remain attached form a favorable surface for regrowth. Growths required at least 4 days to recover perceptibly when conditions were favorable. After heavy shock treatment, periods as long as 3 months were required before regrowth necessitated another treatment. Heavy shock treatments with sodium hypochlorite also increased effluent pH slightly (from 7.1 to 8.2). Regrowth slimes were similar in nature to those initially present.

The application of copper sulfate, in continuous dosages of 3.0 p.p.m. (0.75 p.p.m. as Cu), or shock doses of 36 p.p.m. (9 p.p.m. as Cu) to chlorinated effluent did not improve slime control further.

Copper sulfate alone, in continuous or shock doses, was ineffective.

GENERAL DISCUSSION

The fact that the separator growths were abundant and adsorb oil should indicate their potential application as a biological finishing treatment for refinery effluent. Biological growths are known to be effective in removing oil as well as B.O.D. when applied to trickling filters at concentrations below 100 p.p.m. of oil. Possibly greater concentrations of oil could be tolerated by these acclimatized refinery growths. The mechanism of oil removal by biological growths is not definitely known, but is prob-

ably due to adsorption and actual oxidation of some of the hydrocarbons.

A significant point brought out by the laboratory studies was that growth on continuously submerged surfaces in effluent of low dissolved oxygen was generally greater than with spray application or alternate submergence and exposure. Results suggest that more growth would adsorb larger amounts of oil and greater removals might be attained by the use of submerged contact beds than with conventional trickling filters now recommended for finishing treatments. Further investigation of the use of such growths for finishing treatments of refinery wastes appears warranted.

CONCLUSIONS

Biological growths were found in all parts of petroleum refinery waste systems but were not of significance at all refineries.

Abundant growths were to two types: filamentous blue-green algae (Oscillatoria) and bacterial zoogloea or slimes (primarily Gram-negative short rods), and only the latter were considered objectionable.

The waste component stimulatory to slime growth was barometric condenser water. Reduced sulfur compounds and petroleum hydrocarbons in this waste were stimulatory factors in an environment of low-level dissolved oxygen.

The objectionable effect of slimes in refinery effluents was their adsorption of oil and subsequent liberation of it as a visible film upon deterioration of the growth in the receiving water.

Refinery slime growths were most effectively controlled by liquid chlorine or sodium hypochlorite applied in sufficient quantities to produce a residual. Intermittent daily chlorination producing a residual still detectable after 15 minutes' contact produced effective control.

LITERATURE CITED

(1) American Public Health Association, New York, "Standard Methods for the Examination of Water and Sewage," 9th ed., 1946.
(2) Newcombe, C. L., Trans. Am. Microscop. Soc., 68, No. 4, 355–61 (1949).
(3) Rudolfs, W., and E. S. Crosby, "Effect of Detergents on Slime Growth in Sewers," Division of Water, Sewage and Sanitation Chemistry, Symposium on Detergents in Water, Sewage, and Sanitation Problems, 119th Meeting, AMERICAN CHEMICAL SOCIETY, Cleveland, Ohio, 1951.

Treatment of Refinery Emulsions and Chemical Wastes

CECIL PHILLIPS, JR., Humble Oil and Refining Co., Baytown, Tex.

QUALITY control of the waste water discharged from a large petroleum refinery to prevent undesirable contamination of public waters is a complex chemical problem. Although many of the waste disposal problems encountered are more or less common to the industry, others may be unique to a particular refinery because of differences in its processing operations. This paper discusses a method for improving the quality of a number of emulsions and spent chemical wastes before discharging them

into the effluent from the Baytown, Tex., refinery of the Humble Oil and Refining Co.

The best approach to an over-all program for the improvement in quality of wastes from a particular refinery must be guided by such local considerations as the chemical nature of the wastes produced from the various processing operations, the extent of segregation of objectionable wastes from relatively harmless waste waters, the characteristics of the body of water into which the

Major contributors to the poor condition of waste waters from petroleum refineries are naphthenic and sulfonic acids, either as free acids or as converted water-soluble salts in the sewer systems. These oily salts or soaps form oil-water emulsions that clog gravity-type separators. Water from crude oil de-salters contains high concentrations of calcium and magnesium salts, which in an alkaline medium precipitate in the sewers and function as finely divided solid emulsion stabilizers. Other wastes also contain large quantities of solids which have a marked degrading effect on the quality of the effluent. Upgrading waste water at the Baytown refinery of the Humble Oil and Refining Co. is accomplished by collecting, acidifying, settling chemical wastes in an impounding basin to remove organic materials, neutralizing with lime, clarifying in a standard flocculation step, and filtering the settled sludge.

waste stream is discharged, and the effect of various contaminants on the quality of the receiving body of water that would impair its usefulness to others.

The objectionable materials usually present in the liquid wastes from petroleum refining operations include oil, both free and emulsified; acid or alkaline solutions; inorganic salts; organic acids and phenols or soaps of these compounds; suspended solids that increase the turbidity of the water; and various phenolic, naphthenic and organic sulfur and nitrogen compounds that are toxic to marine life and impart disagreeable tastes and odors to the water (1). In addition many of these materials may be oxidized by dissolved oxygen; accordingly, if they are present in the wastes in a sufficient concentration, they can contribute to an immediate oxygen demand. Some of the materials in the wastes may contribute to a high biochemical oxygen demand. If included in the refinery effluent, these materials can result in the depletion of the dissolved oxygen content of the receiving body of water and interfere with the natural chemical and biological processes necessary to maintain the quality of the water. In addition these wastes produce undesirable effects within the refinery. They decrease efficiency of the gravity-type separators used for recovery of oil from the waste waters as a result of discharging waste streams containing emulsions or emulsion stabilizing materials into the effluent stream flowing through the separators. Another undesirable effect is the recovery of increased volumes of stable emulsions that require separate treatment for their resolution.

One of the principal sources of waste materials that must be disposed of in a refinery is the spent chemical solutions and wash waters resulting from the chemical treating operations on the various hydrocarbon fractions necessary to produce a large variety of petroleum products meeting required quality specifications. Some of these refining steps involve the use of sulfuric acid, phosphoric acid, sodium hydroxide, sodium carbonate, clays, catalysts, and various solvents, such as phenol and liquid sulfur dioxide. The treatment of the wastes from these operations to prevent the formation and stabilization of emulsions in the refinery drainage system, and to eliminate their undesirable effect on the quality of the effluent water discharged from the refinery is an expensive but essential undertaking.

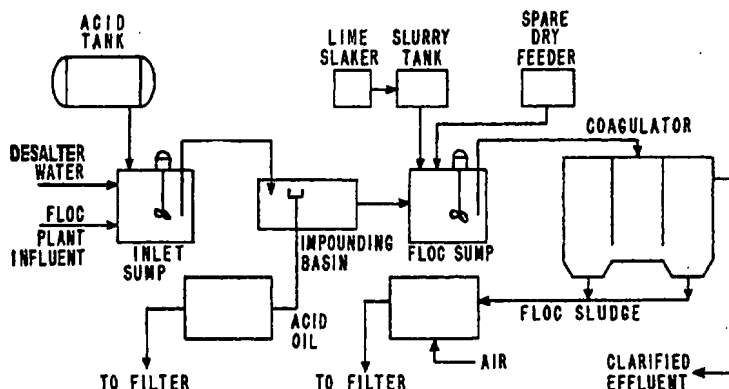### SOURCE AND CHARACTERISTICS OF CHEMICAL WASTES

As part of an over-all effluent improvement program initiated at Humble's Baytown refinery in 1947 a study was made of possible methods for treating a number of spent chemical waste streams. A survey of the liquid wastes in the refinery indicated that although these spent chemical wastes constituted only a relatively small part of the total volume of effluent water leaving the refinery, they contained the major portion of objectionable materials from the standpoint of stabilization and formation of emulsions in the drainage system, and were a potential source of undesirable characteristics in the effluent.

The sources, volumes, and constituents of spent chemical wastes considered in this study are shown in Table I. These wastes include the acidic wash waters from naphthas, heating oil, solvents, kerosine, and lubricating oils after treatment with sulfuric acid; and more concentrated acid wastes from leakage and spills in a process area where acid sludge from various acid treating operations is hydrolyzed for acid recovery. These acid waste waters in general contain varying amounts of emulsified or entrained oil; sulfuric, sulfurous, naphthenic, and sulfonic acids; and tarry resinous materials carried over with the oil from the acid-treating operation and removed in the wash water. In addition these wastes include several spent caustic solutions derived from the neutralization operation following some of the foregoing acid treating steps. The spent caustic solutions contain emulsified oil and sodium soaps of naphthenic acids (3, 5), sulfonic acids, phenols, cresols, and xylenols, all of which are effective emulsion stabilizers (4). These solutions also contain sodium sulfite and thiosulfates which together with some of the organic materials present have a high oxygen demand. The caustic wastes produced in sweetening naphthas, solvents, and middle distillates with sodium hypochlorite solution, and the resolution of emulsions from barometric condensers on crude oil distillation units contain soaps of naphthenic and sulfonic acids and emulsified oil. Another waste stream is the brine discharged from the electrical desalters at the crude oil distillation units. This waste contains high concentrations of calcium and magnesium salts which may precipitate insoluble inorganic salts of these metals upon mixing

TABLE I. SOURCES AND CHARACTERISTICS OF CHEMICAL WASTES

Source	Contaminants	Volume of Waste, Gallons/Day
Wash water from acid treated thermally cracked naphtha		221,000
Wash water from acid treated aliphatic and aromatic solvents	Sulfuric, sulfurous and sulfonic acids, acid sludge, emulsified oil, suspended solids	90,000
Wash water from acid treated lubricating oils		84,000
Wash water from acid treated catalytically cracked naphthas		70,000
Spills and leaks from acid sludge hydrolysis operations		38,000
Wash water from acid treated cracked naphtha bottoms	Sodium salts of naphthenic acids, phenols and fatty acids; suspended solids, emulsified oil	150,000
Spent caustic from resolution of emulsions formed in barometric condensers on crude pipe stills	Sodium salts of naphthenic acids, emulsified oil, sodium hydroxide	150,000
Brine from electrical desalters at crude distillation units	Inorganic calcium, magnesium and iron salts, emulsified oil, suspended solids	386,000
Spent caustic from hypochlorite sweetening of naphthas	Emulsified oil, sodium sulfonates, sodium hydroxide	60,000
Miscellaneous spent caustic	Sodium naphthenates and phenolates, emulsified oil, sodium sulfite, sodium hydroxide	1,000
Total volume		1,250,000

in the drainage system with alkaline waters, or precipitate as insoluble soaps with organic acids from other waste sources. Either of these reactions provide finely divided solids in suspension that readily form and stabilize oil-water emulsions.

Figure 1. Flow Diagram of Flocculation Plant

The organic materials present in these wastes consist of a complex mixture of chemical compounds covering a broad range of molecular weights and structures within any one compound type. This is necessarily so because of the nature of the crude petroleum itself, and the many hydrocarbon fractions that are treated with the various chemical treating agents. As a result of this complexity the organic materials within any one compound type such as phenols or sulfonates exhibit widely varying physical and chemical properties, thus increasing the difficulty of removing these materials from the waste waters.

TREATMENT OF COMBINED CHEMICALS

A laboratory investigation revealed that a great many of the waste waters and spent chemicals could be blended together and treated effectively as a combined waste stream rather than trying to treat each separately. Certain advantages in initial investment and operating costs are immediately apparent from this approach to the waste treatment problem. Since some of the wastes are quite acidic while others are excessively alkaline, a treating system that would take advantage of this fact in using the alkalinity available in some of the wastes to neutralize the acids contained in the remaining wastes was desirable from an economic standpoint.

The process developed for handling these combined wastes is a variation of the conventional clarification treatment usually applied to surface waters to render them suitable for a domestic water supply and consists of three major steps:

The first is the gathering, mixing, acidification (if necessary), and settling of the composite mixture of chemical wastes. This step provides the necessary retention time to allow the maximum reaction and settling of the combined wastes so that the optimum removal of oil and oil-soluble organic materials may be made. This gravity separation in the acid state provides a water of uniform composition with a very low concentration of insoluble organic materials for further treatment.

The second or flocculation step consists of the addition of neutralizing and coagulating chemicals with adequate mixing and settling of sludge from the clarified water.

The third major step is the removal, dewatering, and disposal of the settled sludge from the flocculation step.

A process similar to the one described has been reported by Schindler (6) for the treatment of waste water containing petroleum sulfonic acids from the manufacture of white oils.

In carrying out the over-all effluent improvement program at the Baytown refinery, a separate gathering system was installed

to collect the various spent chemical wastes and a plant was built to clarify these combined wastes using the treating process described. Photo on page 283 shows the spent chemical treating plant with the impounding basin partially filled in the foreground and the cylindrical concrete coagulator on the right behind the impounding basin. The building in the background houses three rotary vacuum precoat filters used for the filtration of emulsions and sediment recovered from the refinery separators, and the flocculation sludge and acid oil emulsions produced in the spent chemical waste treating plant.

A simplified flow diagram of the flocculation plant is shown in Figure 1. The spent chemical wastes are collected and discharged into an earthen impounding basin providing a retention time of approximately one day; thus insuring a feed water of relatively uniform composition to the flocculation equipment. Although the composite waste water normally has a pH between 1 and 3, facilities were provided for the addition of sulfuric acid, on automatic pH control, to the influent stream in a mixing sump ahead of the impounding basin in order that an acid condition could be maintained at all times and thus prevent precipitation of organic and inorganic salts of calcium and magnesium. In this pH range, the soaps of the naphthenic acids and phenolic-type compounds are converted to the original acids and phenols which, except for a few low molecular weight compounds, are essentially insoluble in the water. These acidic compounds along with hydrocarbons released from emulsions that are resolved by the acidification of the combined wastes float to the surface and are removed. The acid oil skimmed from the impounding basin is accumulated for filtration through a rotary vacuum precoat filter for the resolution of emulsions. The oil recovered from the impounding basin amounts to about 90 barrels per day; after filtration, this oil is suitable for use as a component of fuel oil. Water from the impounding basin flows by gravity into a sump where lime is added on automatic pH control to raise the pH of the water to 8.5 to 9 for flocculation. The composition of the mixed waste waters normally is such that treatment with lime alone will produce satisfactory flocculation; a chemical feeder has been provided, however, for the introduction of an additional flocculating agent, such as iron sulfate or alum, if it is required for effective clarification. The solids which precipitate consist principally of calcium and magnesium sulfonates and iron hydroxide. The iron compounds are present in the desalter brines and some of the other waste streams and thus provide a source of natural flocculating agent in the water. After the addition of lime, the waste water is pumped to the inner section of a concrete coagulator where reaction of the lime is completed and the precipitated floc is coagulated by gentle agitation with a motor driven mixer. From the inner section of the coagulator the water flows downward along with the flocculated solids and is discharged into an outer annular section of the coagulator for settling. The clarified water from the outer section flows upward and is discharged from the top of the coagulator to the refinery sewer system. Settled sludge containing approximately 5% by weight of solids is withdrawn from the bottom of the outer annular section of the clarifier to storage tanks prior to filtration. The sludge is dewatered on a vacuum precoat filter and the dry filter cake is disposed of by discarding it along with spent contact clay. A precoat of diatomaceous earth is used for the filtration of the flocculation sludge.

The chemical wastes treating plant was designed for a maximum capacity of 1,500,000 gallons per day, and it has been in operation for more than two years processing slightly more than 1,000,000 gallons per day of mixed wastes listed in Table I. The lime con-

sumption has averaged 3.8 tons per day, and by control of the rate of discharge of some of the more alkaline caustic wastes it has been possible to discontinue the addition of acid to the inlet sump. Because of the corrosive nature of the combined spent chemical wastes, ceramic, brass, and lead-lined materials of construction were employed throughout the plant up to the flocculation sump. Beyond this point steel and concrete were used. The filter for processing the acid oil emulsion was constructed of Monel with brass lines and pumps and lead-lined charge and filtrate tanks.

The design of the plant restricts the spent chemical charge to nonsulfide-bearing wastes because of the potential safety hazard from the evolution of hydrogen sulfide from the acidic solutions if sulfides were present. The major portion of sulfide bearing wastes are now being handled by concentration for sale to an outside company and by acidification followed by stripping in an enclosed tower for recovery of hydrogen sulfide.

The treatment of the concentrated spent chemical wastes through this plant eliminates the undesirable effects of the contaminants on the total refinery effluent. Table II shows the improvements in quality of the chemical waste realized through this treatment. The excess acid in the combined wastes is neutralized from a pH range of 2 to 3 to a slightly alkaline effluent with a pH range of 8 to 9. Major reductions are shown for turbidity, suspended solids, and oil content. The combined wastes entering contain no dissolved oxygen. The concentration of contaminants that contribute to the immediate oxygen demand is reduced from a value of about 6 p.p.m. on the influent stream to a level such that the dissolved oxygen varies from an immediate oxygen demand of 1 p.p.m. to a dissolved oxygen content of 1.4 p.p.m. The chemical oxygen demand as determined by the cold permanganate procedure (2) showed a small reduction—from 125 p.p.m. on the influent to 97 p.p.m. on the clarified effluent. This is believed to be due to the presence of low molecular weight sulfonates and organic acids that are not precipitated in the flocculation step and remain in the clarified effluent.

TABLE II. EFFECT OF FLOCCULATION ON QUALITY OF CHEMICAL WASTES

	Impounding Basin		Coagulator
	Entering	Leaving	Effluent
pH	1–11	2–3	8–9
Turbidity	300–3000	300–1000	15–50
Suspended solids	200	30–50	5–20
Oil	3200	10–50	<5
Dissolved oxygen	0	0	0–1.4
Immediate oxygen demand	6.1	5.9	0–1
Chemical oxygen demand	125	125	97

One of the most significant improvements resulting from the treatment of the spent chemical wastes has been the reduction in volume of stable oil-water emulsions recovered from the main refinery separator due to the removal of the emulsion forming and stabilizing materials from the chemical wastes. This emulsion has been reduced from approximately 2000 barrels per day prior to treatment of the wastes to a current level of about 300 barrels per day. Previously these emulsions were treated with emulsion breaking chemicals for the recovery of dry oil. This treatment was not satisfactory because of incomplete separation. The stable interfacial emulsion and water and sediment layers re-

maining constituted another waste disposal problem. The smaller volume of emulsions currently recovered is resolved satisfactorily by filtration through a diatomaceous earth precoat on a rotary vacuum filter followed by hot settling.

Because of the nature of the processing operations in which the chemical wastes are produced, the concentrations of acid and alkaline materials—principally sulfuric acid and sodium hydroxide—in the combined waste entering the impounding basin varies widely. Occasionally this variation is great enough to allow the stream leaving the impounding basin to become either too acidic or too alkaline. When the pH of this stream falls below 2 the quantity of calcium sulfate formed from the neutralization of the acid with lime is greater than the solubility of this salt and calcium sulfate in the form of gypsum is precipitated and deposited throughout the flocculation system. When the pH of the impounding basin effluent rises above 3.5 to 4, weakly acidic organic materials, such as naphthenic acids and phenols, are not released in the impounding basin; these materials carry through into the flocculation system where they are precipitated as gummy, calcium soaps that foul pumps, lines, and control instruments in this system. Occasional down times on the coagulator have been necessary to remove these deposits mechanically from the equipment. Alterations are in progress to eliminate these difficulties by segregating a number of the spent caustic wastes that contain no naphthenates or phenolates, and adding these alkaline wastes on automatic pH control to the impounding basin effluent stream in a separate mixing sump upstream from the lime addition point. The addition of spent caustic wastes at this point will result in the impounding basin being maintained at a lower average pH level and allow more complete separation of organic acids from the water in the basin. Also more efficient utilization of the available alkalinity in the spent caustic for the neutralization of the acid should be realized due to the more uniform composition of the combined wastes leaving the impounding basin. Control of the pH of the effluent from the impounding basin at a minimum value of 2.5 to 3 by the caustic addition should eliminate the subsequent deposition of calcium sulfate salt in the flocculation equipment.

LITERATURE CITED

(1) Am. Petroleum Inst., New York, "Manual on Disposal of Refinery Wastes, Chemical Wastes," 2nd ed., 1951.
(2) Am. Public Health Assoc., 1790 Broadway, New York, N. Y., "Standard Methods for the Examination of Water and Sewage," 9th ed., pp. 123, 127 (1946).
(3) Gallo, S. G., Carlson, C. S., and Biribauer, F. A., IND. ENG. CHEM., 44, 2610–15 (1952).
(4) Kalichevsky, V. A., and Stagner, B. A., "Chemical Refining of Petroleum," 2nd ed., New York, Reinhold Publishing Corp., pp. 153, 167 (1942).
(5) Lochte, H. L., IND. ENG. CHEM., 44, 2597–2601 (1952).
(6) Schindler, H., Petroleum Processing, 6, No. 5, 492 (1951).

Influence of pH and Water Content on the Type and Stability of Acidic Crude Oil Emulsions[†]

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Dependent upon the conditions of pH and water content, an acidic crude oil may form different type of emulsions with different stability. These oils generally contain large amounts of naphthenic acids, RCOOH, which result from crude oil biodegradation. They also contain heavier compounds such as asphaltenes and resins. All of these amphiphiles may contribute to the formation and stability of emulsions. In this work, an acidic crude oil (total acid number = 1.25) was distilled in three fractions to separate naphthenic acids from resins and asphaltenes. The influence of pH and water content on the type and stability of emulsions prepared with the crude oil and its fractions was investigated. The role of the light, intermediate, and heavy amphiphiles present in the crude oil on its emulsifying properties has been discussed by comparing the emulsion type and stability diagrams obtained for the different oil phases. It has been found that the type of emulsion is governed by the acidic amphiphiles contained in the intermediate fraction. The stability of oil-in-water emulsions is ensured by electrostatic repulsion between the naphthenates, RCOO⁻, present at the interface, whereas that of water-in-oil emulsions is due to the amphiphiles contained in the heavy fraction, i.e., asphaltenes and resins.

Introduction

The decline of conventional oil reserves has led petroleum companies to produce oils with lower American Petroleum Institute (API) degrees. Acidic crude oils belong to the heavy oil family, and many fields have recently been discovered in West Africa, the North Sea, and Venezuela. These oils are biodegraded and contain large amounts of naphthenic acids. This term is referred to as any RCOOH hydrocarbon, where R normally represents the naphthene moiety consisting of cyclopentane and cyclohexane derivatives.[1] However, in regard to petroleum language, the term "R" also accounts for aliphatic chains and aromatics.[2]

The exploitation of acidic oils gives rise to several challenges all along the production line. Reservoir waters are naturally saturated with carbon dioxide (CO_2) in equilibrium with bicarbonate anions (HCO_3^-). During the oil production process, the pH increases because of the pressure drops and the degassing of CO_2 generates $RCOO^-$ naphthenates, which can form salts with the cations present in the reservoir water. Naphthenic acids and their salts are surface-active compounds. They favor the

formation of emulsions and are responsible for a lot of water/crude oil separation difficulties.[3] The plugging of production facilities by scale has been encountered with some acidic oils.[4] The scale is generally a mixture of calcium naphthenates associated with other minerals such as calcium carbonate or clays. It has recently been discovered that the calcium naphthenate scale is primarily composed of the calcium salt of a tetraacid.[5] Naphthenic acids have also been identified to cause corrosion damages on transport and refinery equipments.[6] Last, the contamination of waters by acids of low molecular weight poses severe environmental problems.[7]

In the present work, we have been interested in the emulsifying properties of acidic oils. Several papers dealing with this topic have already been published.[3,8–10] Nevertheless, the general behavior of acidic crude oils and, in particular, the role of naphthenic acids in the formation and stabilization of emulsions are still subject to discussion for the following

(1) Brient, J. A.; Wessner, P. J.; Doyle, M. N. Encyclopedia of Chemical Technology, 4th ed.; Kroschwitz, J. I., Ed.; John Wiley and Sons: New York, 1995; pp 1017–1029.
(2) Hsu, C. S.; Dechert, G. J.; Robbins, W. K.; Fukuda, E. K. Energy Fuels 2000, 14, 217–223.
(3) Hurtevent, C.; Rousseau, G.; Bourrel, M.; Brocart, B. Emulsions and Emulsion Stability, 2nd ed.; Sjöblom, J., Ed.; Taylor and Francis Group: U.K., 2006; pp 477–516.
(4) Goldszal, A.; Hurtevent, C.; Rousseau, G. In Proceedings of the SPE 4th International Symposium on Oilfield Scale; Aberdeen, U.K., January 2002; SPE 874661.
(5) Baugh, T.; Wolf, N. O.; Mediaas, H.; Vindstad, J. E. Paper presented in the 228th ACS National Meeting Division of Petroleum Chemistry, Philadelphia, PA, 2004.
(6) Slavcheva, E.; Shone, B.; Turnbull, A. Br. Corros. J. 1999, 34, 125–131.
(7) Leung, S. S.; MacKinnon, M. D.; Smith, R. E. H. Aquat. Toxicol. 2003, 62, 11–26.
(8) Strassner, J. E. J. Pet. Technol. 1968, 20, 303–312.
(9) Acevedo, S.; Escobar, G.; Ranaudo, M. A.; Khazen, J.; Borges, B.; Pereira, J. C.; Méndez, B. Energy Fuels 1999, 13, 333–335.
(10) Ovalles, C.; Garcia, M. d. C.; Lujano, E.; Aular, W.; Bermudez, R.; Cotte, E. Fuel 1998, 77, 121–126.

Table 1. Analysis of the Oil Phases

system	content (wt %)	TAN (mg of KOH/g)	API°	saturates (wt %)	aromatics (wt %)	resins (wt %)	asphaltenes[a] (wt %)
crude oil	100	1.25	23.6	52.5	32	14.5	1
375[−]	41.5	1.8	34.9	74	26	0	0
375−520	26.7	1.45	20.6	55.9	37.8	6.3	0
520[+]	31.8	0.34	11.4	21.2	35.3	40.8	2.7

[a] Defined as the insoluble fraction in *n*-heptane.

reasons: (i) Naphthenic acids are complex mixtures of RCOOH. For instance, 1500 acids with boiling points ranging from 250 to 350 °C were identified in a California crude oil;[11] (ii) The interfacial activity of RCOOH is pH-dependent.[12,13] Actually, the lightest molecules are readily dissolved in water at neutral pH, whereas the heaviest molecules are mainly oil-soluble. However, most of these molecules can be dissolved in water or present at the water/oil interface at higher pH. Different works performed on *model systems* consisting of solvents (heptane, toluene, or their mixture) and model acids (fatty acids, *trans*-4-pentylcyclohexane-carboxylic acid, or 5-β-cholanic acid) have shown that RCOOH molecules do not stabilize *water-in-oil (w/o) emulsions*, whereas $RCOO^-$ anions enhance the stability of *oil-in-water (o/w) emulsions* by electrostatic repulsions;[14,15] (iii) The interfacial activity of $RCOO^-$ salts depends upon the valence and the concentration of cations (M^{n+}) present in the aqueous phase. A transition of their properties from hydrophilic to lipophilic with the increase of the ionic strength is generally observed.[16] The stabilization of *w/o emulsions* by lipophilic naphthenates $(RCOO^-)_n M^{n+}$ seems to be related to their ability to form lamellar liquid crystalline (LLC) phases around the water droplets;[14,15,17−19] (iv) Acidic oils contain other indigenous surfactants such as resins and asphaltenes. These compounds do not correspond to well-defined chemical families but are defined as solubility classes: asphaltenes are the fraction of the crude oil precipitating in light alkanes (from pentane to heptane), and resins are the fraction of the crude oil soluble in light alkanes but insoluble in liquid propane. It is now well-established that asphaltenes form and stabilize *w/o emulsions*.[20−22] Resins play a role in solvating (or dispersing) asphaltenes and, thereby, influence the stability of w/o emulsions.[23] McLean and Kilpatrick[24] observed that, when the resin/asphaltene mass ratio was varied from 0 to several units, the stability of emulsions first increased, passed through a maximum, and then decreased.

Actually, the complexity of the topic results from the fact that a huge amount of indigenous surfactants with potentially antagonistic effects are present in acidic crude oils. In this work, an acidic crude oil was distilled in three fractions to separate naphthenic acids from resins and asphaltenes. First, the influence of pH on both naphthenate formation and water/oil interfacial tension was studied for a non-emulsified system composed of the acidic crude oil and different water phases. Then, the emulsifying properties of the crude oil were determined for different pH and water contents and compared with those obtained for the fractions to evaluate the role of each surfactant family (naphthenic acids, naphthenates, resins, and asphaltenes) in the type and stability of emulsions.

Experimental Section

Materials. A West African acidic crude oil supplied by Total was chosen for this study. The crude oil was separated in three fractions by two successive fractional distillations performed at reduced pressure and temperatures below 350 °C to prevent thermal

cracking.[25] The light fraction was obtained from the first distillation carried out at a final boiling point (FBP) of 183 °C and a pressure of 2 mmHg. It corresponds to a FBP of 375 °C at atmospheric pressure. That is why this fraction was referred to as 375[−]. The intermediate fraction 375−520 was obtained from the second distillation carried out at a FBP of 292 °C and a pressure of 0.3 mmHg. The residuum of the second distillation constituted the heavy fraction 520[+].

The analysis of each oil phase consisted of (i) measuring the total acid number (TAN), which corresponds to the mass of KOH in milligrams necessary to neutralize the acids contained in 1 g of oil (ASTM D664), (ii) determining the API degree (ASTM D1298), and (iii) performing a SARA (saturates, aromatics, resins, and asphaltenes) characterization. All of the results are given in Table 1.

From the data listed in Table 1, one can notice that the crude oil belongs to the intermediate oil family because its API degree is comprised between 20 and 35. It shows a moderate acidity of 1.25 mg of KOH/g with naphthenic acids mainly present in the light (1.8 mg of KOH/g) and intermediate (1.45 mg of KOH/g) fractions. It contains significant amounts of resins (14.5 wt %) and asphaltenes (1 wt %). Resins are essentially found in the heavy fraction, whereas asphaltenes are only present in this fraction. Consequently, the separation of naphthenic acids from resins and asphaltenes can be considered as reached.

Deionized water was produced by the Millipore Milli-Q 185 E system (conductivity $<10^{-1}$ μS/cm). This aqueous phase, so-called "pure water", had a pH_i (pH of the aqueous phase before the contact with the oil phase) of about 6.5. Alkaline waters were prepared by adding sodium hydroxide pellets (purchased from Prolabo, purity of 98%) to pure water.

A Meterlab PHM 220 equipped with a D31M106 combined pH electrode was used to measure the pH of solutions. Three calibration points for pH (4, 7, and 10) were performed from radiometer analytical buffer solutions. A pH measurement required a minimal amount of water of about 10 mL.

Interfacial Tension. Interfacial tension measurements were performed with an oscillating pendent drop tensiometer from IT Concept, at room temperature. An oil drop was formed and

(11) Seifert, W. K.; Howells, W. G. *Anal. Chem.* 1969, *41*, 554−562.

(12) Rudin, J.; Wasan, D. T. *Colloids Surf.* 1992, *68*, 67−79.

(13) Rudin, J.; Wasan, D. T. *Colloids Surf.* 1992, *68*, 81−94.

(14) Havre, T. E.; Sjöblom, J. *Colloids Surf.* 2003, *228*, 131−142.

(15) Ese, M. H.; Kilpatrick, P. K. *J. Dispersion Sci. Technol.* 2004, *25*, 253−261.

(16) Mendez, Z.; Anton, R. E.; Salager, J. L. *J. Dispersion Sci. Technol.* 1999, *20*, 883−892.

(17) Horváth-Szabó, G.; Czarnecki, J.; Masliyah, J. *J. Colloid Interface Sci.* 2001, *236*, 233−241.

(18) Horváth-Szabó, G.; Masliyah, J. H.; Czarnecki, J. *J. Colloid Interface Sci.* 2001, *242*, 247−254.

(19) Horváth-Szabó, G.; Czarnecki, J.; Masliyah, J. *J. Colloid Interface Sci.* 2003, *257*, 299−309.

(20) Yarranton, H. W.; Hussein, H.; Masliyah, J. H. *J. Colloid Interface Sci.* 2000, *228*, 52−63.

(21) Ali, M. F.; Alqam, M. H. *Fuel* 2000, *79*, 1309−1316.

(22) Dicharry, C.; Arla, D.; Sinquin, A.; Graciaa, A.; Bouriat, P. *J. Colloid Interface Sci.* 2006, *297*, 785−791.

(23) Mouraille, O.; Skodvin, T.; Sjöblom, J.; Peytavy, J. L. *J. Dispersion Sci. Technol.* 1998, *19*, 339−367.

(24) McLean, J. D.; Kilpatrick, P. K. *J. Colloid Interface Sci.* 1997, *196*, 23−34.

(25) Del Bianco, A.; Panariti, N.; Anelli, M.; Beltrame, P. L.; Carniti, P. *Fuel* 1993, *72*, 75−80.

Table 2. Amount of Resolved Water (wt %) from the Bottle-Test and Centrifugation Methods[a]

time	pH$_i$ 6.5		pH$_i$ 12		pH$_i$ 13	
	bottle test	centrifugation	bottle test	centrifugation	bottle test	centrifugation
1 week	0	0	0	12	0	27
2 weeks	0		0		0	5
3 months	0		50		70	
6 months	0		100		100	

[a] Water/oil emulsions were formed with the acidic crude oil for different pH$_i$ and a water content of 30 wt %.

maintained vertically at the end of an inverted needle in a transparent and thermoregulated cell containing the aqueous phase at the desired pH$_i$. Images of the drop were recorded in real time with a camera fitted with a charge-coupled device image sensor (CCD camera), and the interfacial tension was calculated from the drop profile and phase density.

Emulsions. Emulsions were prepared by stirring the crude oil with an Ultra-Turrax T25 homogenizer, at 8000 rpm for 2 min, while slowly pouring the water on it at ambient temperature.

The type of emulsion was determined by adding drops of the emulsion to both pure water and pure heptane. If the drops readily dispersed in water and not in heptane, the emulsion was identified as an o/w emulsion. On the contrary case, the emulsion was identified as a w/o emulsion. Although o/w/o (or w/o/w) multiple emulsions can form for low water (or oil) contents, we did not try to identify them.

The classical method to quantify the stability of an emulsion is to measure the amount of resolved water as a function of time with bottle tests. This method presents the advantage to mimic the natural aging of emulsion. Nevertheless, preliminary tests carried out on emulsions obtained with the crude oil and different aqueous phases showed that several weeks or months were necessary to measure significant differences in stability. To reduce the time for quantifying the emulsion stability, 1-week-aged emulsions were centrifuged at 6000 rpm for 30 min and the amount of resolved water was measured. We verified that this procedure gave the same tendency as that obtained with the bottle-test method (Table 2).

Emulsion Type and Stability Diagrams. The water content (w) and pH value of produced water may vary from one oil field to another and with time for a given oil field. For that reason, we studied the emulsifying properties of the oil phases for different values of these parameters.

Because of the difficulty in recovering enough of free water (see Table 2) to measure pH$_f$ (equilibrium pH of the aqueous phase after the contact with the oil phase), all of the diagrams have been plotted as a function of pH$_i$. For each couple of points (w, pH$_i$), the type and stability of emulsion were determined and reported on a two-dimensional diagram. The criterion used to classify the emulsion stability was (i) *very stable* (+ + +), less than 5 wt % of free water; (ii) *stable* (− + +), between 5 and 50 wt % of free water; (iii) *unstable* (− − +), between 50 and 95 wt % of free water; and (iv) *very unstable* (− − −), more than 95 wt % of free water.

Results and Discussion

Naphthenate Formation. RCOO⁻ were generated from the reaction between the naphthenic acids, RCOOH, and the hydroxide ions, OH⁻, contained in the oil phase and the NaOH solution, respectively.

$$RCOOH + OH^- \rightleftharpoons RCOO^- + H_2O \qquad (R1)$$

According to the reaction R1, the concentration of OH⁻ in the aqueous phase decreases with the formation of RCOO⁻. Therefore, pH$_f$ should be lower than pH$_i$ whenever naphthenates are formed. To evaluate the range of pH$_i$ for which reaction R1 occurs, pH$_f$ was measured for systems composed of equal
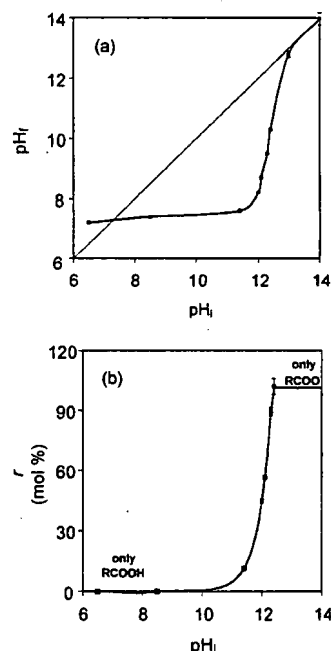
Figure 1. (a) Final pH (pH$_f$) of the aqueous phase as a function of the initial pH (pH$_i$) for a water content, w, of 50 wt % and (b) formation rate of RCOO⁻ calculated from eq 2.

amounts of crude oil and water with different pH$_i$ in contact under gentle stirring (to avoid the formation of stable emulsions) for 3 weeks. Figure 1a shows that pH$_f$ was lower than pH$_i$ for all pH$_i$ between about 7 and 13. For pH$_i$ greater than 13, pH$_i$ and pH$_f$ were nearly equal, suggesting that most naphthenic acids present in the crude oil were converted into naphthenates. The point obtained for pH$_i$ 6.5 appeared as an exception to the general tendency because in this case, pH$_f$ was greater than pH$_i$. Such a behavior has already been reported by Hurtevent et al.[3] for two acidic oils and has been attributed to the basic compounds present in crude oils. A total base number (TBN, ASTM D974) determination for our crude oil gave a value of 2.8 mg of KOH/g, which confirms the presence of basic compounds.

From an industrial point of view, it is interesting to know what ranges of pH are most relevant to oil-field production conditions. The pH value of the produced water, which corresponds to pH$_f$ in our experiments, depends upon many factors, such as the origin of the crude oil, its TAN (i.e., the amount of available RCOOH), the molecular weights of RCOOH (i.e., the biodegradation degree of the crude oil), the water content, the bicarbonate concentration, and the nature and concentration of salts present in water. Few data on the pH value of produced waters are available in the literature.[26,27] However, it seems that the pH value is usually lower than 9, which, in our work, corresponds to an initial pH (pH$_i$) lower than about 12.4. Although very high basic conditions (pH$_i$ > 13) are probably not encountered in oil-field production, the investigation of such conditions will provide information on the effect of salt (sodium naphthenates) on the emulsifying properties of the crude oil (see paragraph entitled "Emulsion Type and Stability Diagram for the Acidic Crude Oil").

(26) Vinstad, J. E.; Bye, A. S.; Grande, K. V.; Hustad, B. M.; Hustvedt, E.; Nergard, B. In *Proceedings of the SPE 5th International Symposium on Oilfield Scale*; Aberdeen, U.K., January 2003; SPE 80375.

(27) Rousseau, G.; Zhou, H.; Hurtevent, C. In *Proceedings of the SPE 3th International Symposium on Oilfield Scale*; Aberdeen, U.K., January 2001; SPE 68307.
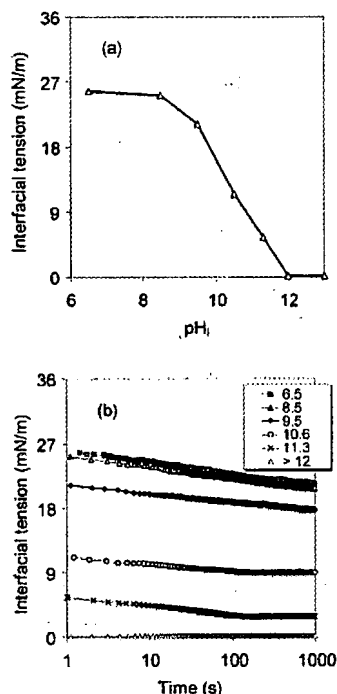
Figure 2. (a) Initial tension of the water/acidic crude oil interface as a function of pH$_i$ and (b) the corresponding tension versus time.

The formation rate of RCOO$^-$ was calculated as the molar ratio of RCOO$^-$ to the total acids RCOOH$_{init}$ initially present in the crude oil:

$$r = \frac{RCOO^-}{RCOOH_{init}} \times 100 \qquad (1)$$

The concentration of RCOO$^-$ was deduced from the difference between pH$_i$ and pH$_f$, whereas that of RCOOH$_{init}$ was obtained from the TAN of the crude oil. Under these conditions, eq 1 gives

$$r = \frac{(10^{pH_i-14} - 10^{pH_f-14})}{TAN/M_{KOH}} \times \frac{w}{100 - w} \times 100 \qquad (2)$$

where M_{KOH} and w represent the molar mass of potassium hydroxide and the water content (wt %) in the system, respectively.

The variation of r versus pH$_i$ for a water content, w, of 50 wt % is represented in Figure 1b. Below pH$_i$ 10, r is close to 0; i.e., most RCOOH present in the system was not dissociated. The increase of r for pH$_i$ between 10 and 12.4 corresponds to the gradual conversion of RCOOH into RCOO$^-$. Beyond 12.4, r is equal to 100, which means that all RCOOH present in the crude oil was converted into RCOO$^-$.

The continuous line in Figure 1b represents the variation of r assuming reaction R1 to be complete; i.e., all OH$^-$ present in the aqueous phase reacted with RCOOH to form RCOO$^-$. With this hypothesis, the term containing pH$_f$ in eq 2 can be neglected. Because the line goes through all of the experimental points, it means that the reaction between naphthenic acids and hydroxide ions can be considered as complete. The same conclusion may be drawn for emulsified systems, because the very large water/oil interface formed under strong stirring conditions should favor the contact between RCOOH located in the oil-phase and OH$^-$ from the aqueous phase.

Water/Crude Oil Interfacial Tension. Figure 2a shows the initial interfacial tension between the acidic crude oil and the

aqueous phase for different pH$_i$. For pH$_i$ lower than 9, the tension remained at a constant value of about 25 mN/m. For pH$_i$ higher than 9, the tension steadily decreased and then reached very small values for pH$_i$ greater than 12. Additional tests performed with a spinning drop tensiometer showed that the interfacial tension for pH$_i$ between 12 and 13 was lower than 0.1 mN/m.

If Figure 2a is compared with Figure 1b, one can notice that a strong correlation exists between the RCOO$^-$ formation and the interfacial tension profile. The constant tension observed at low pH$_i$ corresponded to the system in which almost no RCOO$^-$ was present. The large decrease in tension observed for pH$_i$ between 9 and 12 corresponded to the increasing amount of RCOO$^-$ in the system. For pH$_i$ of 12 and higher, the tension was extremely low, because of a maximum adsorption of RCOO$^-$ at the water/oil interface.

For each pH$_i$, the variation of the interfacial tension as a function of time is given in Figure 2b. For all systems, the tension exhibited a decrease of several units during the first 100 s because of the diffusion of the surface-active molecules from the bulk oil phase to the water/oil interface. Subsequently and dependent upon the value of pH$_i$, different behaviors could be observed. For pH$_i$ of 10.6 and higher, the tension leveled off, suggesting the saturation of the interface by RCOO$^-$. Both the plateau was reached sooner and the equilibrium interfacial tension was lower as pH$_i$ increased. For pH$_i$ of 9.5 and lower, the tension decreased slowly without reaching a plateau during the time allowed for the experiment. At these conditions of pH$_i$, the amphiphiles likely to be present at the interface were naphthenic acids, resins, and asphaltenes. It has already been observed that the reorganization of asphaltenes at the interface could lead to a slow decrease in interfacial tension over a long period of time ($\approx 10^2 - 10^5$ s).[28,29] Jeribi et al.[28] have shown that the kinetics of reorganization of asphaltenes dissolved in model solvents (toluene/heptane mixtures) could be fitted by a monoexponential law. Using their model for our systems, we found that the characteristic times for the reorganization process were comprised between 400 and 500 s for pH$_i$ 6.5, 8.5, and 9.5. These values are in the same order of magnitude as those calculated by Jeribi et al. (1100 s for 1 wt % of asphaltene dissolved in a 50:50 by weight toluene/heptane solution), suggesting the presence of asphaltenes at the interface in our systems. The lower value obtained in our case probably results from the difference in the solvent quality between the acidic crude oil used in this work and that of the model mixture. In particular, the presence of resins can strongly affect the time for adsorption and reorganization of asphaltenes at the water/oil interface.

Emulsion Type and Stability Diagram for the Acidic Crude Oil. The emulsifying properties of the acidic crude oil were studied for the water contents (w) of 10, 30, and 50 wt % and for pH$_i$ between 6.5 and 14. For pH$_i$ between 6.5 and 10.5, the step of variation for pH$_i$ was 2 units. Above pH$_i$ 10.5, the step was reduced to 0.5 units because this pH$_i$ zone corresponded to a significant RCOO$^-$ formation (Figure 1b). The diagram obtained for the crude oil (Figure 3a) shows that most of the emulsions formed within the investigated range of pH$_i$ and w were of the w/o type. As a general rule, the most stable w/o emulsions were obtained for the lowest pH$_i$ and emulsion stability decreased as pH$_i$ increased. A narrow o/w emulsion

(28) Jeribi, M.; Almir-Assad, B.; Langevin, D.; Henaut, I.; Argillier, J.-F. *J. Colloid Interface Sci.* 2002, *256*, 268−272.

(29) Poteau, S.; Argillier, J.-F.; Langevin, D.; Pincet, F.; Perez, E. *Energy Fuels* 2005, *19*, 1337−1341.
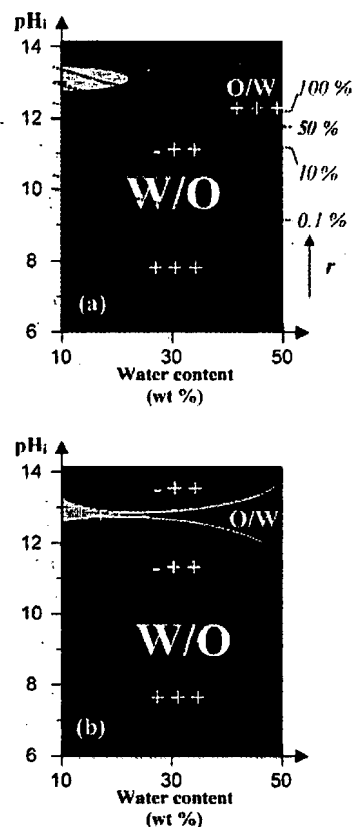
Figure 3. (a) Emulsion type and stability diagram for the acidic crude oil and (b) the corresponding extrapolated diagram. The dotted lines in a correspond to the formation rate of RCOO⁻, r, calculated from eq 2.

region could be observed for w of about 50 wt % and pH$_i$ between 12 and 13.5. These o/w emulsions exhibited a very high stability.

The dotted lines in Figure 3a represent the formation rate of RCOO⁻ (r) calculated from eq 2 for the different pH$_i$ and w. As long as r was lower than 0.1% (i.e., almost no RCOO⁻ was formed), very stable w/o emulsions were obtained. Under these conditions, naphthenic acids, resins, and asphaltenes could be responsible for the high stability of the w/o emulsions.

For r between 0.1 and 50%, the decrease in stability observed for the w/o emulsions can be attributed to the increasing amount of RCOO⁻ present in the system.

For r of about 50%, a strong decrease in stability for the w/o emulsions and the formation of o/w emulsions were observed for w of 10 and 50 wt %, respectively. In this case, RCOO⁻ were predominant at the water/oil interface and the repulsive electrostatic interactions between naphthenate polar heads tended to turn the curvature of the interface toward the oil phase. As a result, if the system contained a sufficient amount of water, o/w emulsions formed. In the contrary case, w/o emulsions were unstable. Actually, because of the low amount of water, the clearest w/o emulsion zone in Figure 3a probably contained o/w/o multiple emulsions. For the intermediate water content of 30 wt %, we did not observe either a minimum in stability for the w/o emulsions or a zone of o/w emulsions. In fact, as illustrated by the extrapolated diagram in Figure 3b, these two zones probably existed and would certainly have been detected if we had used a narrower screening step for pH$_i$.[30]

(30) Salager, J.-L.; Briceno, I.; Bracho, C. L. *Encyclopedic Handbook of Emulsion Technology*; Sjöblom, J., Ed.; Marcel Dekker: New York, 2001; pp 455–495.
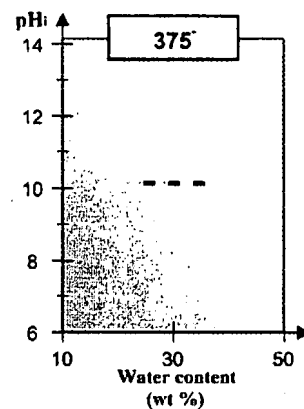
Figure 4. Emulsion type and stability diagram for the 375⁻ fraction.

For r "greater than" 100%, i.e., when all RCOOH present in the system reacted with OH⁻ to form RCOO⁻, a second inversion in the emulsion type (from o/w to w/o) could be observed for w of 50 wt %. This inversion can be attributed to a "salt effect" as already pointed out by Mendez et al.[16] Actually, in all experiments, pH$_i$ was fixed with sodium hydroxide. Under these conditions, a variation of pH$_i$ from 13 to 14 led to an increase in the Na⁺ concentration from 0.1 to 1 mol/L. At high pH, Na⁺ cations screened the electrostatic repulsion between the naphthenate polar heads and thereby reduced their specific area. As a consequence, the curvature of the interface had a tendency to turn toward water, and dependent upon the water/oil ratio, w/o emulsions could be formed. This salt effect was probably also responsible for the strengthening of the w/o emulsion stability observed for w of 10 wt %. The formation of a liquid crystal layer composed mainly of sodium naphthenates on the water/oil interface might also explain the increase in stability of the w/o emulsions. However, microscopic observations between crossed polarizers of w/o emulsions formed at pH$_i$ of 14 did not show the birefringent zones usually observed for LLC phases.[15,17]

Emulsion Type and Stability Diagrams for the Fractions. If, on one hand, RCOO⁻ seemed to be the main amphiphile responsible for the formation and stabilization of the o/w emulsions, on the other hand, different lipophilic components were likely to take part in that of the w/o emulsions. These amphiphiles were naphthenic acids, resins, asphaltenes at low pH$_i$, and lipophilic naphthenates at high pH$_i$. With the aim to clarify their contribution but also to determine which RCOO⁻ (light, intermediate, or heavy) was involved in the formation and stabilization of the o/w emulsions, we have confronted the emulsifying properties of the acidic oil to those of the 375⁻, 375–520, and 520⁺ fractions.

Figure 4 shows that the emulsions prepared with the most acidic fraction 375⁻ were *very unstable* for all pH$_i$ and w investigated. In fact, a complete and rapid water/oil separation occurred once the agitation stopped, so that it was not possible to determine the type of emulsion. However, we observed that the aqueous phase took an oil-like coloration for pH$_i$ greater than 10.5 and this coloration was more intense as pH$_i$ increased. Fourier transform infrared spectroscopy (FTIR) measurements showed that the coloration of the aqueous phase coincided with the disappearance of naphthenic acids in the 375⁻ fraction (parts a and b of Figure 5). Therefore, the RCOO⁻ generated from the light fraction was fully soluble in water but was unable to form and stabilize emulsions.

As for the crude oil, the diagram obtained for the 375–520 fraction (Figure 6) shows a narrow zone of stable o/w emulsions
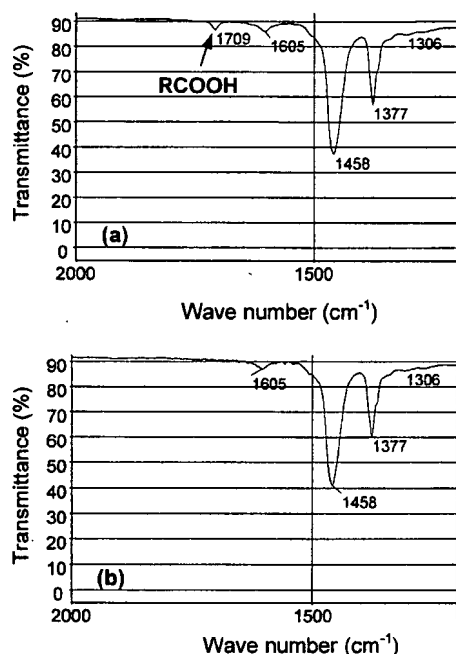
Figure 5. FTIR spectra of the 375^- fraction (a) before and (b) after contacting it with an aqueous phase at pH_i 13 and for $w = 50$ wt %. The band at 1709 cm^{-1} is characteristic of the carbonyl function of naphthenic acids.
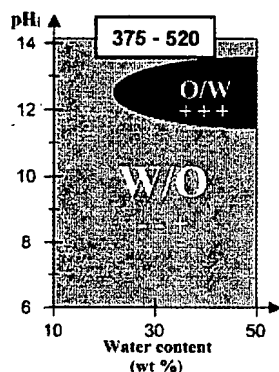

Figure 6. Emulsion type and stability diagram for the 375–520 fraction.

for high pH and w surrounded by a large w/o emulsion zone. Contrary to the w/o emulsions obtained with the crude oil, those formed with this fraction were *unstable* for all conditions of pH_i and w. Actually, the oil/water separation occurred within a few hours. The occurrence of unstable w/o emulsions at low pH_i shows that the naphthenic acids of the 375–520 fraction were not responsible for the high stability of w/o emulsions formed with the crude oil.

The presence of a stable o/w emulsion region in both diagrams strongly suggests that the $RCOO^-$ issue from the intermediate fraction played a major role in the stabilization of the o/w emulsions formed with the crude oil. The extension of this region toward lower water contents results probably from the absence of heavy lipophilic compounds in the 375–520 fraction (see Table 1), which favor w/o emulsion formation.

The transition in the emulsion type from o/w to w/o that occurred at high pH_i and w greater than 30 wt % can be attributed to a salt effect. However, the w/o emulsions were unstable, highlighting the fact that the lipophilic naphthenates formed from the 375–520 fraction did not contribute directly to the stability of oil-continuous emulsions.
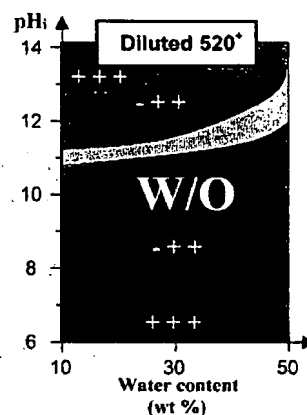
Figure 7. Emulsion type and stability diagram for the 520^+ fraction.

Because the 520^+ fraction was "solid" at ambient temperature, we diluted it in a toluene/heptane solution to reduce its viscosity. The weight proportions of the constituents in the 520^+/toluene/heptane mixture were 32:45:23 wt %. This mixture mimicked the weight contents in saturates and aromatics of the $(375^- + 375–520)$ fractions. Under these conditions, the weight contents in resins and asphaltenes in the diluted 520^+ fraction were similar to those in the crude oil. The dilution led to a decrease in the acidity of the 520^+ fraction from 0.34 to 0.1 mg of KOH/g.

Figure 7 shows that the diluted 520^+ fraction formed w/o emulsions for all conditions of pH_i and w. Several reasons can explain why the water/oil interface could not turn toward the aqueous phase: (i) the low amount of naphthenic acids, (ii) the high molecular weight of the $RCOO^-$, and (iii) the presence of the heaviest lipophilic compounds of the crude oil, i.e., resins and asphaltenes.

The stability of the w/o emulsions was similar to that of the crude oil emulsions over a large range of pH_i and w. Resins and asphaltenes were certainly responsible for this behavior because the crude oil and the 520^+ fraction were the only oil phases that contained significant amounts of these heavy amphiphiles. Using interfacial dilatational rheology measurements, Dicharry et al.[22] have recently shown that these lipophilic compounds were directly involved in the stabilization of w/o emulsions formed with the same crude oil diluted in cyclohexane.

Conclusion

The distillation of the acidic crude oil in three fractions allowed for the separation of the naphthenic acids from resins and asphaltenes. Most acids were contained in the light and intermediate fractions, whereas asphaltenes and resins were essentially present in the heavy fraction. The contribution of the amphiphiles present in an acidic crude oil on the formation and stabilization of emulsions depending upon the water content and initial pH of the aqueous phase has been identified as follows: (i) the light naphthenic acids and naphthenates are unable to form and stabilize emulsions; (ii) the acids contained in the intermediate fraction seem to dictate the type of emulsions formed with the crude oil; (iii) the naphthenates generated from the intermediate fraction are responsible for the formation and stabilization of o/w emulsions formed at high pH and water content; and (iv) the heaviest amphiphiles contained in the crude oil, i.e., resins and asphaltenes, played a major role in the long-term stability of the oil-continuous emulsions.

Petroleum Refining

Technology and Economics

Fourth Edition

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4
Crude Distillation

The crude stills are the first major processing units in the refinery. They are used to separate the crude oils by distillation into fractions according to boiling point so that each of the processing units following will have feedstocks that meet their particular specifications. Higher efficiencies and lower costs are achieved if the crude oil separation is accomplished in two steps: first by fractionating the total crude oil at essentially atmospheric pressure; then by feeding the high-boiling bottoms fraction (topped or atmospheric reduced crude) from the atmospheric still to a second fractionator operated at a high vacuum. (See Photo 2, Appendix E.)

The vacuum still is employed to separate the heavier portion of the crude oil into fractions because the high temperatures necessary to vaporize the topped crude at atmospheric pressure cause thermal cracking to occur, with the resulting loss to dry gas, discoloration of the product, and equipment fouling due to coke formation.

Typical fraction cut points and boiling ranges for atmospheric and vacuum still fractions are given in Tables 4.1 and 4.2.

Relationships among the volume-average, molal-average, and mean-average boiling points of the crude oil fractions are shown in Figure 4.1a and b.

Nitrogen and sulfur contents of petroleum fractions as functions of original crude oil contents are given in Figures 4.2–4.5.

4.1 DESALTING CRUDE OILS

If the salt content of the crude oil is greater than 10 lb/1000 bbl (expressed as NaCl), the crude requires desalting to minimize fouling and corrosion caused by salt deposition on heat transfer surfaces and acids formed by decomposition of

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Note: Throughout this text the symbol M is used to represent 1000 in accordance with standard U.S. engineering practice. For example, MBPSD means 1000 BPSD and MMBtu means 1,000,000 Btu.

Table 4.1 Boiling Ranges of Typical Crude Oil Fractions

Fraction	Boiling ranges, °F	
	ASM	TBP
Butanes and lighter		
Light straight-run naphtha (LSR)	90–220	90–190
Heavy straight-run naphtha (HSR)	180–400	190–380
Kerosine	330–540	380–520
Light gas oil (LGO)	420–640	520–610
Atmospheric gas oil (AGO)	550–830	610–800
Vacuum gas oil (VGO)	750–1050	800–1050
Vacuum reduced crude (VRC)	1050+	1050+

Table 4.2 TBP Cut Points for Various Crude Oil Fractions

Cut	IBP (°F)	EP (°F)	Processing use
LSR gasoline cut	90	180	Min. light gasoline
	90	190	Normal LSR cut
	80	220	Max. LSR cut
HSR gasoline (naphtha)	180	380	Max. reforming cut
	190	330	Max. jet fuel opr.
	220	330	Min. reforming cut
Kerosine	330	520	Max. kerosine cut
	330	480	Max. jet-50 cut
	380	520	Max. gasoline operation
Light gas oil	420	610[a]	Max. diesel fuel
	480	610[a]	Max. jet fuel
	520	610[a]	Max. kerosine
Heavy gas oil (HGO)	610	800	Catalytic cracker or hydrocracker feed
Vacuum gas oil	800	1050	Deasphalter or catalytic cracker feed
	800	950	Catalytic cracker or hydrocracker feed

[a] For maximum No. 2 diesel fuel production, end points as high as 650°F (343°C) can be used.
Note: In some specific locations, economics can dictate that all material between 330°F IBP and 800°F EP (166 to 427°C) be utilized as feed to a hydrocracker.
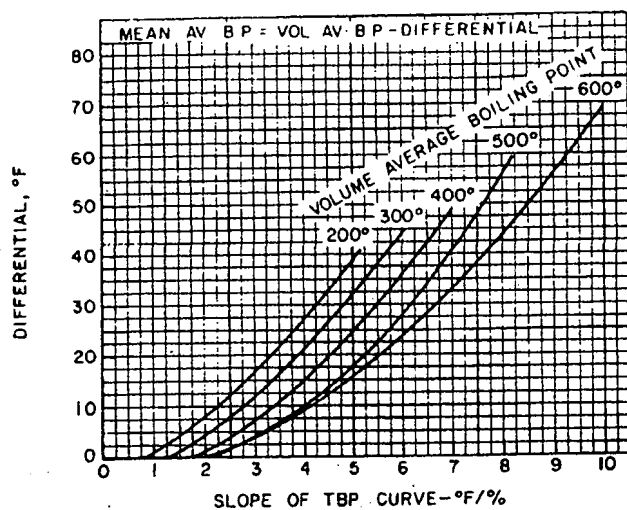
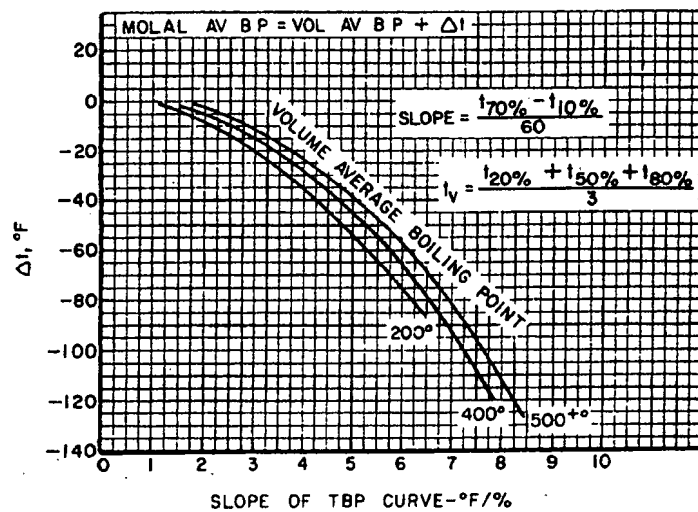**Figure 4.1a** Mean average boiling point of petroleum fractions.

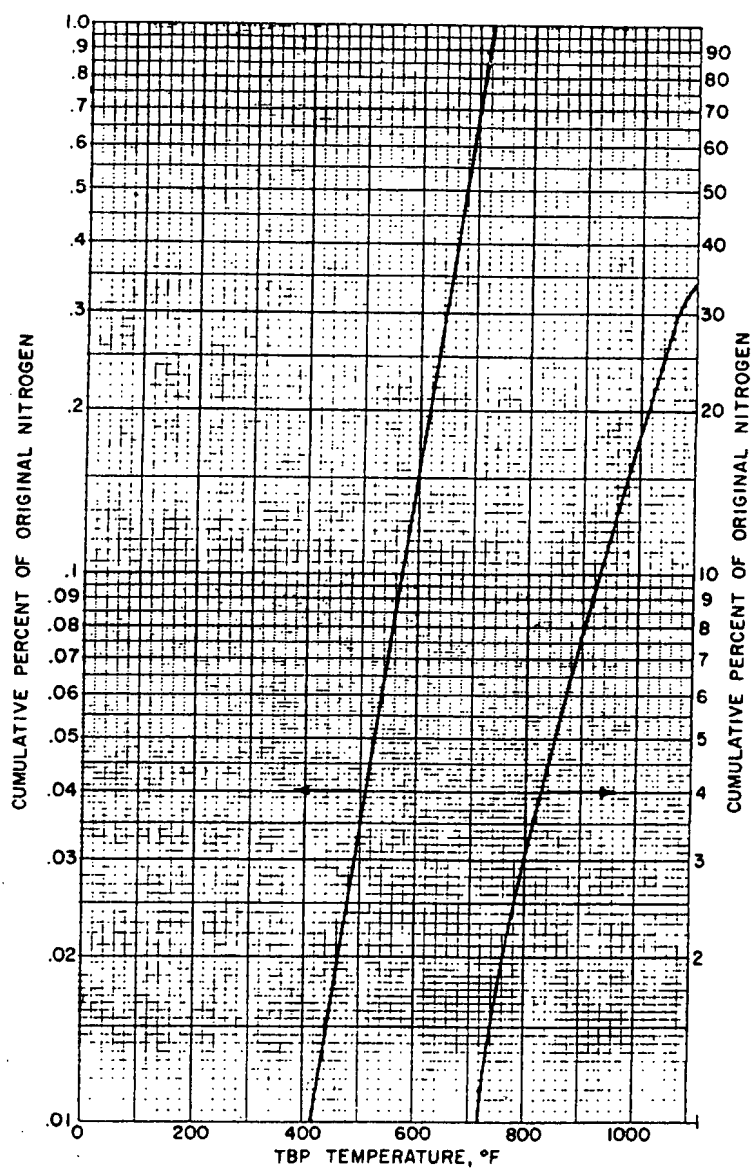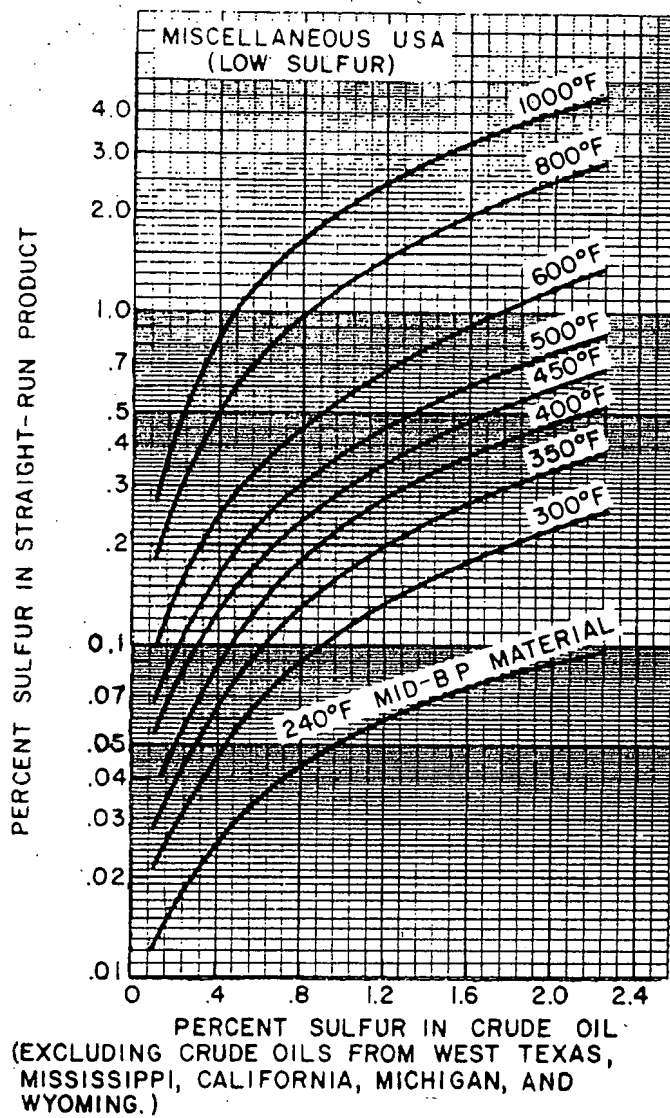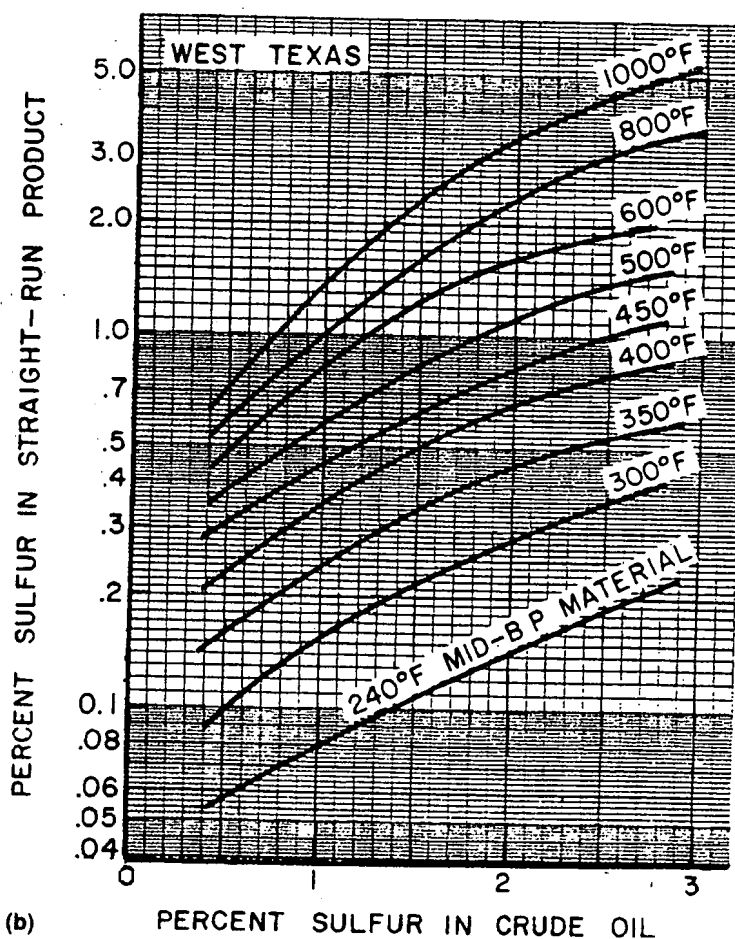**Figure 4.1b** Molal average boiling point of petroleum fractions.

**Figure 4.2** Nitrogen distributions in crude oil fractions.

Figure 4.3a   Sulfur content of products from miscellaneous U.S. crude oils. (From Ref. 5.)

Figure 4.3b Sulfur content of products from West Texas crude oils. (From Ref. 5.)

the chloride salts. In addition, some metals in inorganic compounds dissolved in water emulsified with the crude oil, which can cause catalyst deactivation in catalytic processing units, are partially rejected in the desalting process.

The trend toward running heavier crude oils has increased the importance of efficient desalting of crudes. Until recently, the criterion for desalting crude oils was 10 lb salt/1000 bbl (expressed as NaCl) or more, but now many companies desalt all crude oils. Reduced equipment fouling and corrosion and longer catalyst life provide justification for this additional treatment. Two-stage de-
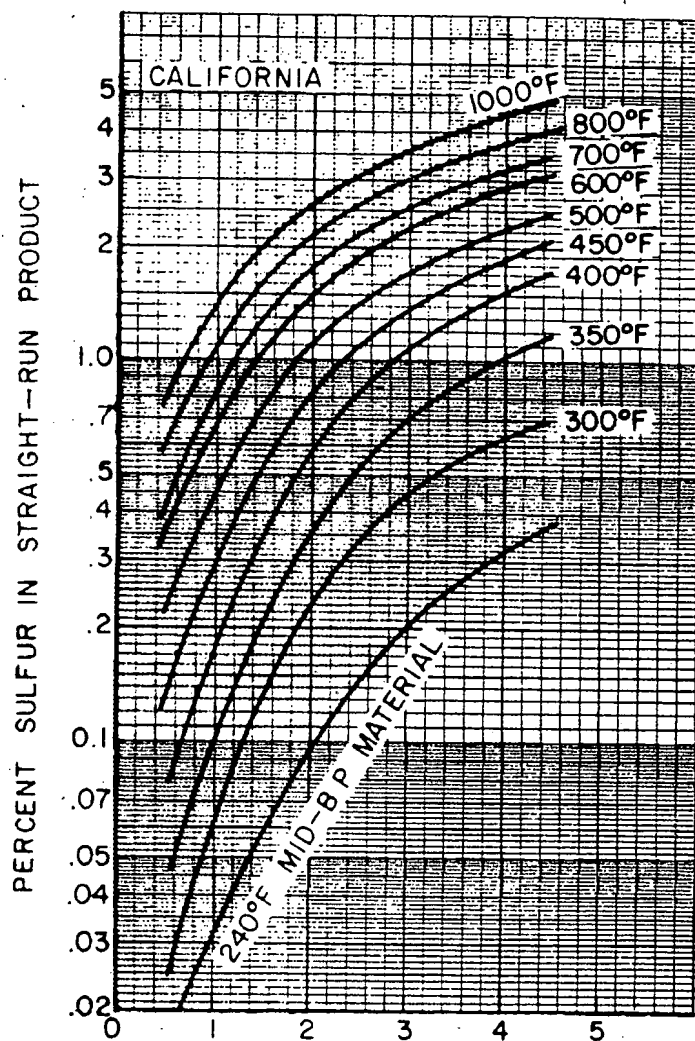
(a)   PERCENT SULFUR IN CRUDE OIL

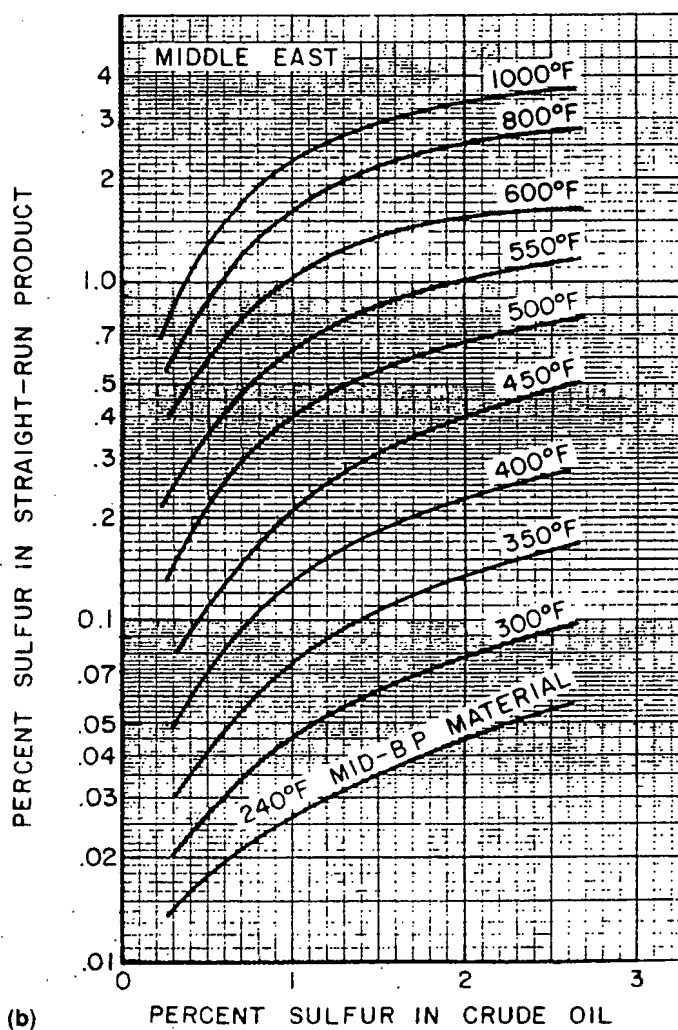**Figure 4.4a**   Sulfur content of products from California crude oils. (From Ref. 5.)

(b)

Figure 4.4b   Sulfur content of products from Middle East crude oils. (From Ref. 5.)
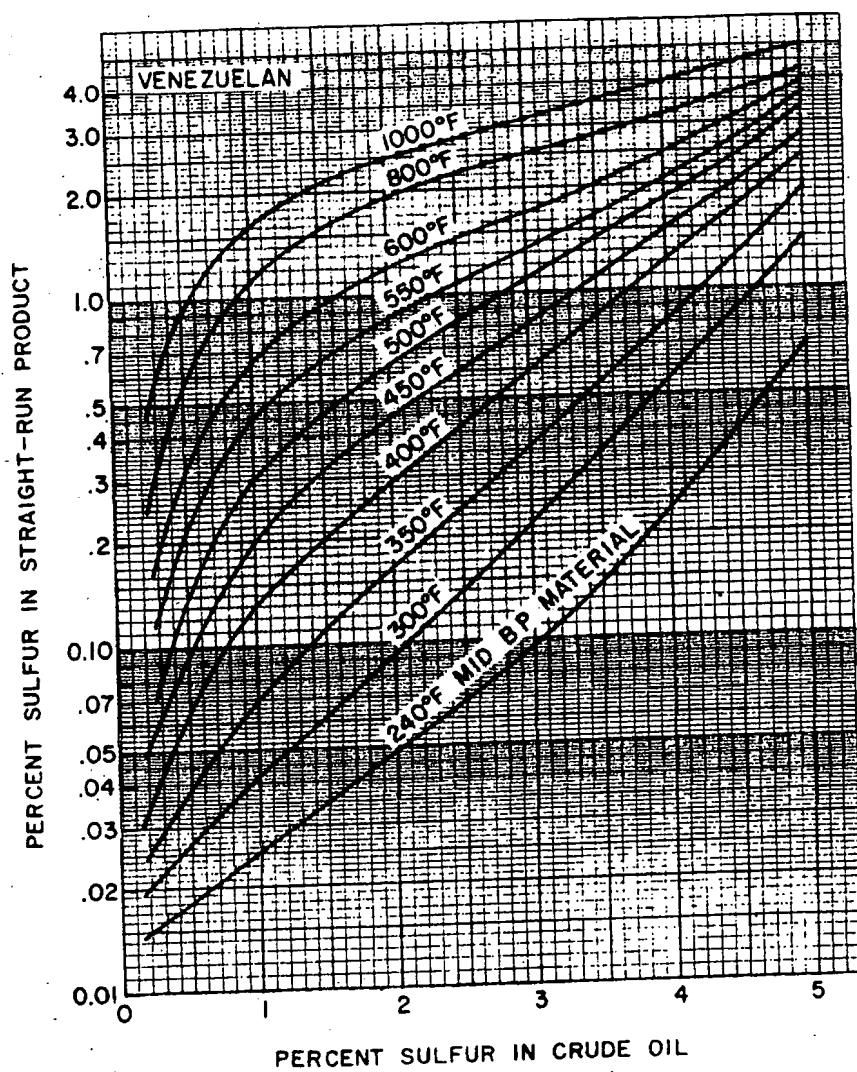
Figure 4.5 Sulfur content of products from Venezuelan crude oils. (From Ref. 5.)

salting is used if the crude oil salt content is more than 20 lb/1000 bbl and, in the cases where residua are catalytically processed. there are some crudes for which three-stage desalting is used.

The salt in the crude is in the form of dissolved or suspended salt crystals in water emulsified with the crude oil. The basic principle is to wash the salt from the crude oil with water. Problems occur in obtaining efficient and economical water/oil mixing, water-wetting of suspended solids, and separation of the wash water from the oil. The pH, gravity, and viscosity of the crude oil, as well as the volume of wash water used per volume of crude, affect the separation ease and efficiency.

A secondary but important function of the desalting process is the removal of suspended solids from the crude oil. These are usually very fine sand. clay, and soil particles; iron oxide and iron sulfide particles from pipelines, tanks. or tankers; and other contaminants picked up in transit or production. Total suspended solids removal should be 60% or better [1] with 80% removal of particles greater than 0.8 micron in size.

Desalting is carried out by mixing the crude oil with from 3 to 10 vol% water at temperatures from 200 to 300°F (90 to 150°C). Both the ratio of the water to oil and the temperature of operation are functions of the density of the oil. Typical operating conditions are [1]:

°API	Water wash, vol%	Temp. °F (°C)
>40	3–4	240–260 (115–125)
30–40	4–7	260–280 (125–140)
<30	7–10	280–330 (140–150)

The salts are dissolved in the wash water and the oil and water phases separated in a settling vessel either by adding chemicals to assist in breaking the emulsion or by developing a high-potential electrical field across the settling vessel to coalesce the droplets of salty water more rapidly (Fig. 4.6). Either AC or DC fields may be used and potentials from 12.000 to 35,000 volts are used to promote coalescence. For single-stage desalting units 90 to 95% efficiencies are obtained and two-stage processes achieve 99% or better efficiency.

One process uses both AC and DC fields to provide high dewatering efficiency. An AC field is applied near the oil–water interface and a DC field in the oil phase above the interface. Efficiencies of up to 99% water removal in a single stage are claimed for the dual field process. About 90% of desalters use AC field separation only.
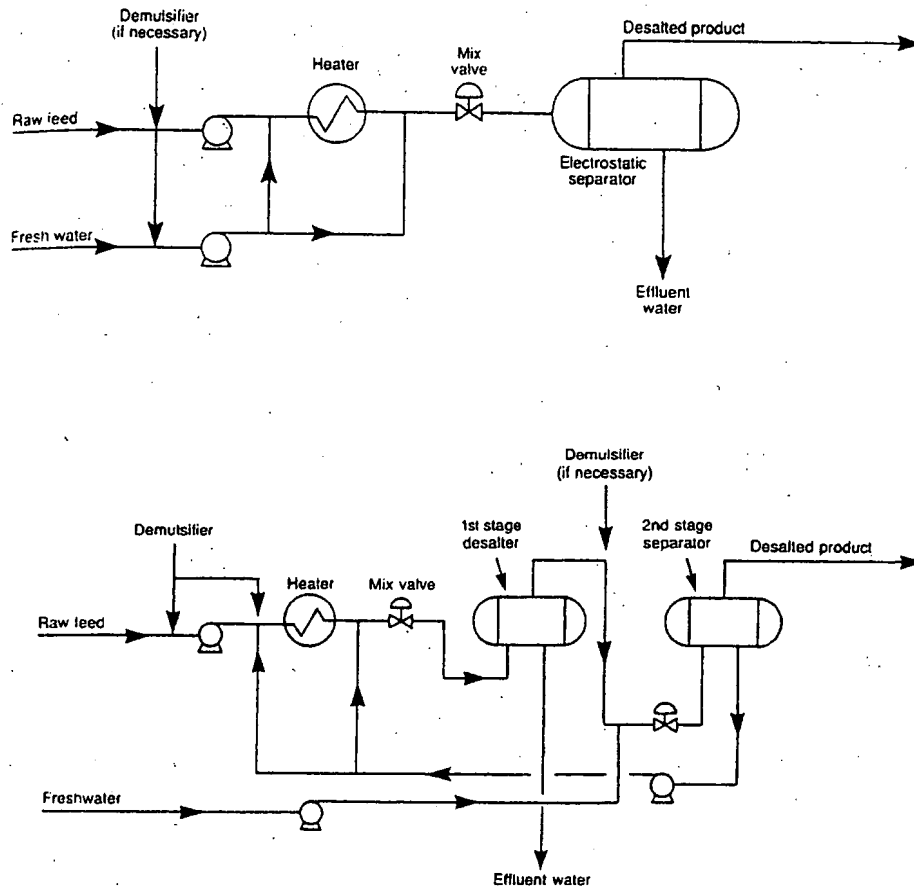
Figure 4.6 Single- and two-stage electrostatic desalting systems. (Flowsheets courtesy of Petrolite Corporation.)

The dual field electrostatic process provides efficient water separation at temperatures lower than the other processes and, as a result, higher energy efficiencies are obtained.

Heavy naphthenic crudes form more stable emulsions than most other crude oils and desalters usually operate at lower efficiencies when handling them. The crude oil densities are close to the density of water and temperature above 280°F (138°C) are needed. It is sometimes necessary to adjust the pH of the brine to obtain pH values of 7 or less in the water. If the pH of the brine exceeds 7,

emulsions can be formed because of the sodium naphthenate and sodium sulfide present. For most crude oils it is desirable to keep the pH below 8.0. Better dehydration is obtained in electrical desalters when they are operated in the pH range of 6 to 8 with the best dehydration obtained at a pH near 6. The pH value is controlled by using another water source or by the addition of acid to the inlet or recycled water.

Make-up water averages 4 to 5% on crude oil charge and is added to the second stage of a two-stage desalter. For very heavy crude oils (<15° API),
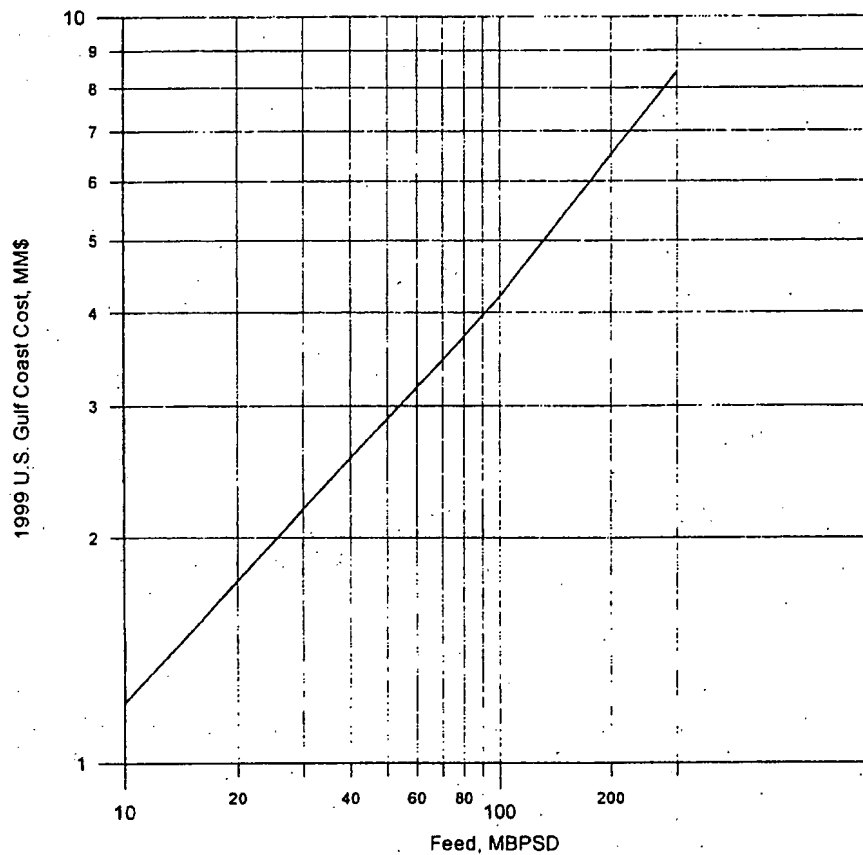
Figure 4.7 Crude oil desalting units investment cost: 1999 U.S. Gulf Coast. (See Table 4.3.)

addition of gas oil as a diluent to the second stage is recommended to provide better separation efficiencies.

Frequently, the wash water used is obtained from the vacuum crude unit barometric condensers or other refinery sources containing phenols. The phenols are preferentially soluble in the crude oil thus reducing the phenol content of the water sent to the refinery waste water handling system.

Suspended solids are one of the major causes of water-in-oil emulsions. Wetting agents are frequently added to improve the water wetting of solids and reduce oil carry-under in desalters. Oxyalkylated alkylphenols and sulfates are the most frequently used wetting agents.

The following analytical methods are used to determine the salt content of crude oils:

1. HACH titration with mercuric nitrate after water extraction of the salt
2. Potentiometric titration after water extraction
3. Mohr titration with silver nitrate after water extraction
4. Potentiometric titration in a mixed solvent
5. Conductivity

Although the conductivity method is the one most widely used for process control, it is probably the least accurate of these methods. Whenever used it should be standardized for each type of crude oil processed.

Table 4.3 Desalter Unit Cost Data

Costs included	
1. Conventional electrostatic desalting unit	
2. Water injection	
3. Caustic injection	
4. Water preheating and cooling	
Costs not included	
1. Waste water treating and disposal	
2. Cooling water and power supply	
Utility data (per bbl feed)	
Power, kWh	0.01–0.02
Water injection, gal (m³)	1–3 (0.004–0.012)
Demulsifier chemical, lb (kg)ᵃ	0.005–0.01 (0.002–0.005)
Caustic, lb (kg)	0.001–0.003 (0.0005–0.0014)

ᵃ 1990 price approximately $1.50/lb.
Note: See Fig. 4.6.

Installed costs of desalting units are shown in Figure 4.7, and utility and chemical requirements are given by Table 4.3.

4.2 ATMOSPHERIC TOPPING UNIT

After desalting, the crude oil is pumped through a series of heat exchangers and its temperature raised to about 550°F (288°C) by heat exchange with product and reflux streams [1,2]. It is then further heated to about 750°F (399°C) in a furnace (i.e., direct-fired heater or "pipe-still") and charged to the flash zone of the atmospheric fractionators. The furnace discharge temperature is sufficiently high [650 to 750°F (343 to 399°C)] to cause vaporization of all products withdrawn above the flash zone plus about 10 to 20% of the bottoms product. This 10 to 20% "over-flash" allows some fractionation to occur on the trays just above the flash zone by providing internal reflux in excess of the sidestream withdrawals.

Reflux is provided by condensing the tower overhead vapors and returning a portion of the liquid to the top of the tower, and by pump-around and pumpback streams lower in the tower. Each of the sidestream products removed from the tower decreases the amount of reflux below the point of drawoff. Maximum reflux and fractionation is obtained by removing all heat at the top of the tower, but this results in an inverted cone-type liquid loading which requires a very large diameter at the top of the tower. To reduce the top diameter of the tower and even the liquid loading over the length of the tower, intermediate heat-removal streams are used to generate reflux below the sidestream removal points. To accomplish this, liquid is removed from the tower, cooled by a heat exchanger, and returned to the tower or, alternatively, a portion of the cooled sidestream may be returned to the tower. This cold stream condenses more of the vapors coming up the lower and thereby increases the reflux below that point.

The energy efficiency of the distillation operation is also improved by using pump-around reflux. If sufficient reflux were produced in the overhead condenser to provide for all sidestream drawoffs as well as the required reflux, all of the heat energy would be exchanged at the bubble-point temperature of the overhead stream. By using pump-around reflux at lower points in the column, the heat transfer temperatures are higher and a higher fraction of the heat energy can be recovered by preheating the feed.

Although crude towers do not normally use reboilers, several trays are generally incorporated below the flash zone and steam is introduced below the bottom tray to strip any remaining gas oil from the liquid in the flash zone and to produce a high-flash-point bottoms. The steam reduces the partial pressure of the hydrocarbons and thus lowers the required vaporization temperature.